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Chemistry

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OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

MEMORANDUM

Date: July 24, 2006

Subject: Quizalofop-P ethyl: New Uses on Barley, Wheat, Sunflower, and Flax. Summary of Analytical Chemistry and Residue Data.

DP Barcode: D266204
EPA Reg. No. 33906-9
40 CFR: §180. 441
MRID Nos.: 44967701 - 05, 45089201 – 03, and 45885801 - 04

Petition No. 0F6076
PC Code: 128709
Pesticide Type: Herbicide

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This residue chemistry summary document (RCSD) was originally prepared under contract by Dynamac Corporation (2275 Research Blvd, Suite 300; Rockville, MD 20850 and has been reviewed by the Health Effects Division (HED)/Office of Pesticide Programs (OPP) to reflect the current policies.

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Executive Summary

Quizalofop ethyl is a selective herbicide currently registered for the control of annual and perennial grasses on noncrop and on crop land areas. The technical quizalofop ethyl is a mixture of R-and S-enantiomers. The pesticidally active isomer is the R-enantiomer (quizalofop-P ethyl) which is the active ingredient (ai) in Targa® herbicide (EPA Reg. No. 33906-9). A 0.88 lb ai/gal emulsifiable concentrate (EC) formulation of Targa® herbicide is registered to Nissan Chemical Industries, Ltd. for use on canola and crambe, cotton, dry beans, mint, legume vegetables, and sugar beets. The petitioner is proposing to amend the label of Targa® herbicide to include uses on barley, flax, sunflower, and wheat. The proposed uses are preplant or preemergence applications to barley and wheat at a maximum seasonal rate of 0.083 lb ai/A, and preemergence or postemergence applications to flax and sunflower at a maximum seasonal rates of 0.165 lb ai/A and 0.124 lb ai/A, respectively. The proposed preharvest intervals (PHIs) are 70 days for flax, and 60 days for sunflower. No PHIs were proposed for barley and wheat.

In conjunction with the proposed new uses, Nissan Chemical Industries, Ltd., has proposed the establishment of permanent tolerances for the combined residues of the herbicide quizalofop-P ethyl ester [ethyl(R)-[2-(4-((6-chloroquinoxalin-2-yl)oxy)phenoxy) propanoate] and its acid metabolite, quizalofop-P [R-2-(4-((6-quinoxalin-2-yl)oxy)phenoxy)propanoic acid] and the S-enantiomers of both the ester and the acid, all expressed as quizalofop-P ethyl ester, in/on the following raw agricultural commodities (RACs):

Barley	0.05 ppm
Flax, seeds	0.05 ppm
Sunflower, seeds	1.9 ppm
Wheat	0.05 ppm

Quizalofop ethyl tolerances are established under 40 CFR §180.441. Tolerances for the combined residues of quizalofop ethyl and quizalofop, expressed as quizalofop ethyl, are established under §180.441(a)(1) in/on commodities including dry and succulent beans and peas, cowpea forage and hay, field pea vines and hay, soybean commodities, and sugar beet roots and tops; tolerance levels range from 0.05 ppm for soybean seed to 3.0 ppm for the forage/vines and hay of cowpea and field pea. Under §180.441(a)(2), tolerances for combined residues of quizalofop ethyl, quizalofop, and quizalofop methyl, expressed as quizalofop ethyl, have been established in eggs, milk, milk fat, and the fat, meat, and meat byproducts of cattle, goat, hog, horse, poultry, and sheep, at 0.01-0.05 ppm. Under §180.441(a)(3), tolerances for the combined residues of quizalofop-P ethyl ester, acid metabolite quizalofop-p, and the S-enantiomers of the ester and the acid, expressed as quizalofop-P ethyl ester, have been established in/on sugar beet molasses, canola meal and seed, cotton seed, lentil seed, and peppermint and spearmint tops at 0.05-2.0 ppm. Time-limited tolerances which expired 6/14/99 were established under §180.441(a)(4) for combined residues of quizalofop-P ethyl ester, acid metabolite quizalofop-p, and the S-enantiomers of the ester and the acid, expressed as quizalofop-P ethyl ester, in/on sugar beet commodities, crop group 6, and crop subgroup 7A. A tolerance with regional registration has been established for combined residues of quizalofop-P ethyl ester, acid metabolite quizalofop-p, and the S-enantiomers of the ester and the acid, expressed as quizalofop-P ethyl ester, in/on pineapple.

The qualitative nature of the residue in plants is adequately understood based on previously submitted plant metabolism studies with soybean, cotton, tomatoes, potatoes, and sugar beets. HED has determined that the residues of concern (ROC) in plant commodities are quizalofop-P ethyl, its acid metabolite quizalofop-P, and the S -enantiomers of both compounds, each expressed as quizalofop-P ethyl. The metabolism studies indicated that quizalofop ethyl does not accumulate but is rapidly hydrolyzed at the ethyl ester to form the quizalofop acid. The acid then undergoes cleavage of the enol ether linkage between the phenyl and quinoxalinyl rings in the acid, and/or cleavage of the ether linkage between the isopropanoic group and the phenyl ring to form phenols. The phenols conjugate with plant sugars; some hydroxylation or further cleavage of the phenols occurs. Metabolism studies with soybeans demonstrated that the racemic mixture of quizalofop ethyl and the R-enantiomer, quizalofop-P ethyl, have nearly identical pathways.

The qualitative nature of the residue in livestock is adequately understood based on metabolism studies with goats and poultry. The studies indicated that quizalofop ethyl is metabolized in livestock via hydrolysis to quizalofop acid which then undergoes methylation to form quizalofop methyl ester. No phenols were detected in either goat or hen commodities, indicating that cleavage of the ether linkages of quizalofop does not occur. The ROC in livestock commodities are quizalofop ethyl, quizalofop-methyl, and quizalofop acid.

The petitioner has proposed that the existing high performance liquid chromatography/ultra violet (HPLC/UV) method used for tolerance enforcement of soybean commodities (Method AMR-153-83, Revision 3) be used for the enforcement of the proposed tolerances in/on barley, flax, sunflower, and wheat commodities. Because the petitioner did not include any validation data reflecting analysis of barley, flax, sunflower, or wheat commodities using the current enforcement method, and because the extraction procedures of the methods used for data collection in the studies submitted with this petition differ significantly from the extraction procedures of the existing enforcement method, HED cannot conclude that the current enforcement method would be adequate for the enforcement of tolerances in/on residues in/on barley, flax, sunflower, or wheat commodities.

Sufficient data have been submitted to support the use of the data-collection methods, HPLC Method No. SARS-98-06 (used for flax and sunflower) and Morse Method Meth-147 (used for barley and wheat), for enforcement purposes, pending petition method validation (PMV). The methods involve hydrolysis of samples with methanolic potassium hydroxide (KOH) to convert quizalofop-P ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). Residues of MeCHQ are partitioned into hexane, and the extract is cleaned up by gel permeation chromatography (GPC) prior to analysis by HPLC using fluorescence detection. The validated limit of quantitation (LOQ) is 0.05 ppm for all matrices. The methods will be forwarded to the BEAD's Analytical Chemistry Branch (ACB) for PMV.

Adequate methods are available for the enforcement of tolerances in/on livestock commodities. HPLC/UV Method AMR-627-86 is available for the determination of residues of quizalofop ethyl, quizalofop acid, and quizalofop-methyl in livestock tissues, and HPLC/UV Method AMR-515-86 (Revision A) is available for determination of residues of quizalofop ethyl, quizalofop acid, and quizalofop-methyl in milk. Methods AMR-627-86 and AMR-515-86 have undergone PMV and have been forwarded to the Food and Drug Administration (FDA) for publication in

the Pesticide Analytical Manual (PAM) Volume II. In addition, HPLC/UV Methods AMR-846-87, AMR-845-87, and AMR-623-86 are available for the determination of residues of quizalofop ethyl, quizalofop acid, and quizalofop-methyl in livestock fat, cream, and eggs, respectively. Methods AMR-846-87, AMR-845-87, and AMR-623-86 have been forwarded to the FDA for publication in PAM Volume II as letter methods.

Multiresidue method data for quizalofop ethyl are available; quizalofop ethyl is completely recovered using Multiresidue Methods Section 302 (Luke Method; Protocol D). No data are available pertaining to recovery of quizalofop acid or quizalofop-methyl using the multiresidue methods.

Adequate storage stability data are available for soybean seed indicating that residues of quizalofop ethyl and quizalofop are stable during up to 48 and 36 months, respectively, of frozen storage. In addition, data are available indicating that residues of quizalofop are relatively stable in/on cotton seed, meal, and oil stored frozen for up to 28 months. Storage stability data included in this petition indicate that residues of quizalofop-P ethyl and quizalofop-P are stable in/on wheat forage, grain, hay, and straw during up to 11-13 months of frozen storage. These data are sufficient to support the storage durations and conditions of samples from the barley, flax, sunflower, and wheat field trials and flax, sunflower, and wheat processing studies.

Adequate ruminant and poultry feeding studies were submitted previously. These studies indicate that tolerances are needed for livestock commodities to support the current and proposed uses of quizalofop-P ethyl. The maximum theoretical dietary burdens (MTDBs) of quizalofop-P ethyl to livestock have been calculated using the registered and proposed uses. Based on the calculated MTDBs, the established tolerances are adequate for all livestock commodities with the exception of milk fat; an increased tolerance of 0.25 ppm should be proposed for milk fat.

The submitted crop field trial data for barley, and wheat are adequate. For barley and wheat, the application rates reflected in the studies (0.068 lb ai/A for both) are less than the proposed maximum (0.083 lb ai/A for both); however, the petitioner has indicated that the application rates used in the crop field trials are the desired application rates. Therefore, label amendments are required to modify the proposed application rates on barley and wheat to reflect the use patterns of the field trials. Combined residues of quizalofop-P ethyl, quizalofop-P, and their S-enantiomers were below the LOQ in/on all samples of barley grain, hay, and straw; flax seed, and wheat forage, grain, hay, and straw. These data indicate that tolerances at the LOQ are appropriate for barley, flax, and wheat commodities. The petitioner should propose separate tolerances in/on barley grain, hay, and straw, and wheat forage, hay, grain, and straw.

Adequate wheat processing studies have been submitted. Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on wheat grain, wheat bran, flour, germ, middlings, and shorts. Since the residues were below the LOQ in all wheat processed commodities, no tolerances are needed for wheat processed commodities. The wheat processing study may be translated to barley.

The submitted crop field trial data for flax are adequate. For sunflower, additional crop field trial data are needed to evaluate residue decline. For flax and sunflower, the studies reflected the

maximum proposed application rates and the proposed PHIs. The maximum combined residues of quizalofop-P ethyl, quizalofop-P, and their S-enantiomers, were 1.32 ppm in/on sunflower seed. Using the tolerance spreadsheet, the recommended tolerance for sunflower seed is 1.9 ppm.

Adequate sunflower processing studies have been submitted. Residues of total quizalofop-P ethyl did not concentrate in sunflower oil but concentrated slightly in sunflower meal. Using the sunflower meal processing factor (1.2x) and the highest average field trial (HAFT) residues in sunflower seed (1.31 ppm), expected residues in sunflower meal would be 1.6 ppm, less than the recommended seed tolerance of 1.9 ppm. A tolerance for quizalofop-P ethyl residues in sunflower meal is not needed. A flax processing study was not conducted because residues were below the LOQ in/on flax seed following treatment at 5x.

The available confined/field rotational crop data indicate that a 120-day plant back interval (PBI) is required for all crops other than those with registered uses.

No Codex MRLs have been established for residues of quizalofop ethyl. Canadian MRLs have been established for residues of quizalofop ethyl and quizalofop in/on several commodities; flax is the only crop included in the subject petition with a Canadian MRL, at 0.05 ppm. No Mexican MRLs have been established for any of the proposed crops.

Note to PM: Nissan Chemical Industries' product (EPA Reg. No. 33906-9) is coded in the Pesticide Product Information System (PPIS) as containing quizalofop ethyl (PC Code 128711) as the active ingredient. The active ingredient in this product is actually the resolved form, quizalofop-P ethyl (PC Code 128709); therefore, PPIS should be corrected.

In addition, the current tolerance expression for livestock commodities, specified in 40 CFR §180.441(a)(2) is for the combined residues of quizalofop, quizalofop ethyl, and quizalofop-methyl, all expressed as quizalofop ethyl. Because the methods used for analysis of livestock commodities reported results in terms of quizalofop and not in terms of quizalofop ethyl, the tolerance expression should be revised as follows:

"Tolerances are established for the combined residues of the herbicide quizalofop (2-[4-(6-chloroquinoxalin-2-yl-oxy)phenoxy]propanoic acid), quizalofop ethyl (ethyl-2-[4-(6-chloroquinoxalin-2-yl-oxy)phenoxy]propanoate), and quizalofop-methyl (methyl 2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propanoate), all expressed as quizalofop, as follows:"

Regulatory Recommendations and Residue Chemistry Deficiencies

Based on HED's examination of the residue chemistry database for quizalofop-P ethyl, pending submission of a revised Section B (see requirements under Directions for Use) and a revised Section F (see requirements under Proposed Tolerances), there are no residue chemistry issues that would preclude granting a conditional registration for the proposed uses on barley, flax, sunflower, and wheat and the establishment of tolerances for combined residues of quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds, all expressed as quizalofop ethyl, as follows:

Barley, grain	0.05 ppm
Barley, hay	0.05 ppm
Barley, straw	0.05 ppm
Flax, seed	0.05 ppm
Sunflower, seed	1.9 ppm
Wheat, forage	0.05 ppm
Wheat, grain	0.05 ppm
Wheat, hay	0.05 ppm
Wheat, straw	0.05 ppm

In addition, a revised tolerance for milk fat of 0.25 ppm should be established.

Registration of the use of Targa® herbicide on wheat, barley, sunflower, and flax should be conditional until the data requirements specified below under Residue Analytical Methods, Multiresidue Methods, and Crop Field Trials have been fulfilled.

HED's recommendation for adding these proposed uses to the label and the corresponding tolerances will be addressed in the quizalofop-P ethyl human health risk assessment.

HED also notes that a new dairy cattle feeding study will be required to support any additional uses of quizalofop ethyl/quizalofop-P ethyl on livestock feed crops.

860.1200 Directions for Use

The following changes are recommended in the draft label of Targa® herbicide:

- All application rates on the label (for both registered and proposed uses) are presented in terms of "oz product/A." The label should be amended to clarify that application rates are in terms of fluid ounces (i.e., liquid measure) and not in terms of weighed ounces.

- Page 2, under "Preplant burn down" add "Do not exceed the maximum recommended rate/acre/season for the crop that is going to be planted when additional applications are made as preplant burn down."

- Page 6, under "Rhizome Johnson grass – Southern States" add "Do not exceed the maximum recommended rate/acre/season for the crop that is going to be planted when additional applications are made to control Rhizome Johnson grass."

- Page 8, under "Spot or Small Area Spray" add the following limitations: " (i) Do not treat >10% of the total treated area as spot/small area treatment and (ii) Do not exceed the maximum recommended rate/acre/season for the crop that is going to be planted when additional applications are made as spot or small area treatment."

- Page 11, "specify a minimum retreatment interval (RTI) for crops on which multiple applications are allowed. For flax and sunflower, the available data support a minimum RTI of 7 days."

- Page 11, revise the maximum use rate of Targa® herbicide at "10 fl. oz." per acre per season for Barley and Wheat. The proposed maximum seasonal rates for barley and wheat of 0.083 lb ai/A are greater than the maximum rates used in the barley and wheat crop field trials of 0.068 lb ai/A. Because the petitioner has stated that the rates used in the crop field trials are the intended maximum seasonal rate, the proposed label should be amended to state that the maximum seasonal application rates for barley and wheat are 0.068 lb ai/A.

- Page 11, the proposed grazing/feeding restrictions are impractical for barley and wheat and should be removed from the product label.

860.1340 Residue Analytical Methods

- HPLC Methods, SARS-98-06 (used for flax and sunflower) and Morse Method Meth-147 (used for barley and wheat) will be forwarded to ACB for PMV. We note that the laboratory doing independent laboratory validation (ILV) has recommended some changes/clarifications to HPLC Method SARS-98-06. Unless ACB concludes differently, the modifications recommended by the ILV laboratory will have to be made to the Method SARS-98-06 prior to its acceptance as a tolerance enforcement method; any additional changes recommended by ACB will also have to be incorporated.

- For both methods, the method descriptions did not address the issue of determination of the S-enantiomers of quizalofop ethyl and quizalofop. Because the KOH hydrolysis step would convert both the R- and S-enantiomers of quizalofop ethyl and quizalofop to MeCHQ, all reported results for total quizalofop-P ethyl residues would include residues of both the R and S enantiomers of quizalofop ethyl and quizalofop. Both methods should be modified to include a statement addressing the inclusion of the S-enantiomers in the method determination, because the S-enantiomers are included in the tolerance expression for quizalofop-P ethyl.

860.1360 Multiresidue Methods

- Multiresidue method data for the metabolites, quizalofop and quizalofop-methyl should be submitted.

860.1500 Crop Field Trials

- A residue decline study should be submitted for sunflower. In the study, (i) samples should be collected at 3 to 5 sampling times in addition to the requested

PHI, (ii) all sampling times should fall within the crop stage when harvesting could reasonably be expected to occur, and (iii) all sampling times should be approximately equally spaced and, where possible, should represent both shorter and longer PHIs than that requested.

860.1550 Proposed Tolerances

- The petitioner proposed tolerances in/on "barley" and "wheat" at 0.05 ppm; separate tolerances in/on barley grain, barley hay, barley straw, wheat forage, wheat grain, wheat hay, and wheat straw should be proposed, each at 0.05 ppm.
- Based on the calculations in the tolerance spreadsheet, the appropriate tolerance level for sunflower seed is 1.9 ppm; a revised tolerance should be proposed.
- The proposed tolerances should be revised to reflect the correct commodity definitions as specified in Table 7.
- The available data indicate that a revised tolerance of 0.25 ppm is needed for milk fat.

Background

Nissan Chemical Industries, Ltd. has submitted a label amendment for Targa® herbicide (EPA Reg. No. 33906-9) for adding new uses on barley, flax, sunflower, and wheat. Targa® herbicide contains quizalofop-P ethyl as the sole ai, which is a R-enantiomer of quizalofop ethyl. Chemically, quizalofop ethyl is a racemic mixture containing R- and S-enantiomers and the former is the pesticidally active component. Quizalofop ethyl is a selective preplant, pre- and postemergence herbicide registered for the control of annual and perennial grasses on noncrop and on crop land areas. Along with the required studies, the petitioner also submitted supplemental information on Food Quality Protection Act (FQPA) requirements (MRID Nos. 44967705 and 45089203).

The chemical structure of quizalofop-P ethyl and its major breakdown products are presented in Table 1 and its physicochemical properties are presented in Table 2.

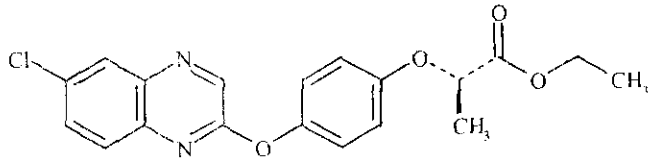
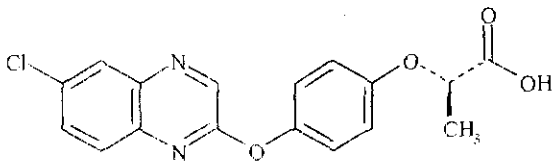
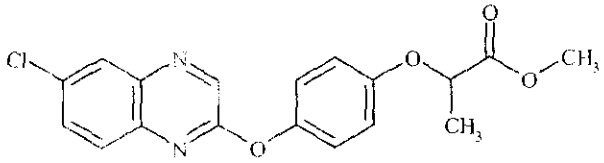
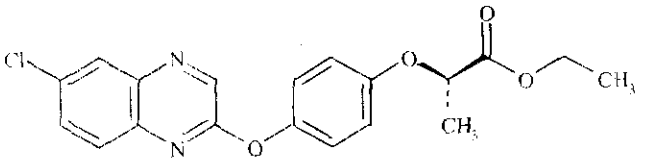
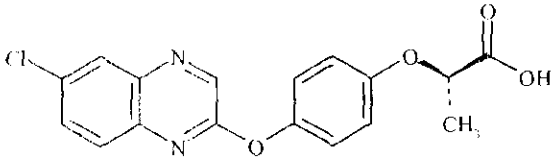
Table 1. Quizalofop-P ethyl Nomenclature.	
Chemical structure	
Common name	Quizalofop-P ethyl
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb ai/gal EC formulation (EPA Reg. No. 33906-9)
Chemical structure of quizalofop-P metabolite	 (2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid
Chemical structure of quizalofop-methyl	 methyl 2-[4-(6-chloroquinoxalin-2-yl-oxy)phenoxy]propanoate
Chemical structure of the S-enantiomer of quizalofop ethyl	 (2S)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
Chemical structure of the S-enantiomer of quizalofop	 (2S)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid

Table 2. Physicochemical Properties of the Technical Grade Test Compound - Quizalofop-P ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	Solvents / g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 *n*-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

860.1200 Directions for Use

Nissan Chemical Industries, Ltd. is proposing a label amendment for the 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Targa® herbicide; EPA Reg. No. 33906-9) for adding new uses on flax, sunflower, barley, and wheat. The currently registered uses include canola, crambe, cotton, dry beans, lentils, mint, dry and succulent peas, snap beans, soybeans, and sugar beets. The use patterns for the proposed new uses are presented in Table 3.

Applications are to be made using ground equipment, in a minimum of 10 gal/A in nonarid areas or 15 gal/A in arid areas, or aerial equipment, in a minimum of 3 gal/A in nonarid areas or 5 gal/A in arid areas. Application through any type of irrigation system is prohibited. The grazing of livestock in treated areas or feeding of forage, hay, or straw from the treated crops to livestock is prohibited. Tank-mix applications may be made with broadleaf herbicides, insecticides, and fungicides. Tank mix products should be registered for use on the specific crop and the most restrictive label directions are to be followed. The label specifies a PBI of 120 days for crops not registered for treatment with quizalofop ethyl.

Table 3. Summary of the Proposed Use Patterns of Quizalofop-P ethyl Formulation.				
Application Timing	Rate/ Appln (lb ai/A)	Max. Rate /Season (lb ai/A) [1]	PHI (days)	Use Patterns and Limitations [2]
Barley				
Preplant or Preemergence	0.017-0.083	0.083	NS [3]	Apply 7 days before planting as a broadcast or banded treatment using ground or aerial equipment. Crop injury may result if applied within 7 days of planting. Adjuvant: petroleum-based crop oil concentrate (COC).
Flax				
Preplant, Pre- or postemergence	0.017-0.165	0.165	70	Apply as a broadcast or banded treatment using ground or aerial equipment. Adjuvant: petroleum-based COC, methylated seed oil, or nonionic surfactant (NIS).
Spot/small area treatment [4]	0.375% v/v solution			Apply directly to target weed in a solution containing a spray adjuvant.
Sunflower				
Preplant, Pre- or postemergence	0.017-0.124	0.124	60	Apply as a broadcast or banded treatment using ground or aerial equipment. Adjuvant: NIS
Spot/small area treatment	0.375% v/v solution			Apply directly to target weed in a solution containing a spray adjuvant.
Wheat				
Preplant or Preemergence	0.017-0.083	0.083	NS	Apply 7 days before planting as a broadcast or banded treatment using ground or aerial equipment. Crop injury may result if applied within 7 days of planting. Adjuvant: petroleum-based COC.

1. Maximum number of applications per season and retreatment intervals (RTIs) were not specified.
2. Aerial and ground applications are in minimum 3 and 10 gal/A of water, respectively.
3. Not specified
4. The spot/small area treatment is spray application of a 0.0375% v/v mixture at 0.017 to 0.034 lb ai/A as an early preplant burn-down to control growing weeds.

Conclusions. The proposed use patterns are adequate to allow evaluation of the residue data submitted in support of this petition. The following label amendments are recommended for clarity and to conform to the field trial data submitted on the proposed crops.

1. The maximum seasonal rate for barley and wheat proposed at 0.083 lb ai/A is greater than the maximum rate of 0.068 lb ai/A used in the barley and wheat crop field trials. Therefore, the draft label should be amended to state that the maximum seasonal application rate to barley and wheat is 0.068 lb ai/A.

2. The petitioner should specify a minimum RTI for crops for which multiple applications are allowed. For flax and sunflower, the available data support a minimum RTI of 7 days.

3. All application rates on the label (for both registered and proposed uses) are presented in terms of "oz product/A." For clarity, the label should be amended to read "fl. oz. product/A."

4. The proposed grazing/feeding restrictions are impractical for barley and wheat and should be removed from the product label.

5. Under the Pre-plant Burndown (page 2), Rhizome Johnson grass - Southern States (page 6), and Spot or Small Area Spray (page 8), a statement should be added not to exceed the seasonal application rate for the crop that is going to be planted. In addition, the spot and small area spray treatment should be limited to not more than 10% of the total cropped area

860.1300 Nature of the Residue - Plants

The nature of the residue in plant commodities is adequately understood based on metabolism studies conducted with soybean, cotton, tomatoes, potatoes, and sugar beets. These studies have been reviewed previously (PP# 1F3951; D160972 and D166083, J. Stokes, 3/4/92; PP# 3F4268; D196041, D196043, D205430, D205432, D206200, D206201, and D212620-D212622, F. Griffith, 3/30/95; and PP# 5F3252, CB No. 1127, M. Firestone, 9/25/85). The metabolism studies indicated that quizalofop ethyl does not accumulate but is rapidly hydrolyzed at the ethyl ester to form the quizalofop acid. The acid then undergoes cleavage of the enol ether linkage between the phenyl and quinoxalinyl rings and/or cleavage of the ether linkage between the isopropanoic group and the phenyl ring to form phenols. Metabolism studies with soybeans demonstrated that the racemic mixture of quizalofop ethyl and the resolved R-enantiomer, quizalofop-P ethyl have nearly identical pathways (D182751, J. Stokes, 7/15/93). The ROC in plant commodities are quizalofop-P ethyl, quizalofop-P (acid metabolite), and S- enantiomers of both the parent and acid, each expressed in terms of quizalofop-P ethyl.

860.1300 Nature of the Residue - Livestock

The nature of the residue in livestock is adequately understood based on metabolism studies with goats and poultry (PP# 5F3252; CB Nos. 2806, 2806, 2810, & 2811, 12/18/87, G. Otakie). The studies indicate that quizalofop ethyl is metabolized in livestock via hydrolysis to quizalofop acid which then undergoes methylation to form quizalofop methyl ester. No phenols were detected in either the goat or hen matrices, indicating that cleavage of the ether linkages of quizalofop does not occur. In hens the quizalofop-P acid is utilized in fatty chain elongation to form quizalofop-pentanoic acid. The ROC in livestock commodities are quizalofop-P ethyl, quizalofop-methyl, and quizalofop-P, each expressed in terms of quizalofop-P ethyl.

860.1340 Residue Analytical Methods – Plant Commodities

44967703 der (Sunflower seed, meal, and oil; includes MRID 44967704)
45885803 der (Alfalfa, barley, and wheat; includes MRID 45885804)

Data Collection Method for Flax and Sunflower Commodities: Nissan Chemical Industries, Ltd., has submitted a method description and validation data for an HPLC method (Method No. SARS-98-06), for the determination of residues of quizalofop-P ethyl and its acid metabolite quizalofop-P in flax seed, sunflower seed, and sunflower processed commodities (meal and oil). The method, or an earlier version (Method No. XAM-38), was used to determine residues of quizalofop-P ethyl and quizalofop-P in/on samples of flax seed, sunflower seed, and sunflower processed commodities from the crop field trials and processing studies associated with this petition. Details of the method are available in the data evaluation record (DER) for MRID 44967703 and 44967704.

The petitioner has proposed the current HPLC/UV enforcement method (DuPont Method AMR-153-83, Revision 3, see below) as a confirmatory method for the HPLC data-collection method.

A successful ILV trial was conducted using samples of sunflower seed fortified with quizalofop-P ethyl and quizalofop-P at 0.05 ppm (LOQ) and 2.0 ppm (proposed tolerance level) each (MRID 44967704). The ILV laboratory recommended some minor changes to the method to improve clarity; it does not appear that the method has been modified to incorporate these recommendations.

No radio validation data were submitted for this method. Because the extraction procedures of the method are relatively rigorous, no radio validation data will be required to support the method.

Data Collection Method for Barley and Wheat Commodities: The petitioner has submitted description and validation data for an HPLC method, Morse Method Meth-147, for the determination of residues of quizalofop-P ethyl and its acid metabolite quizalofop-P in alfalfa, barley, and wheat RACs and wheat processed commodities. This method was used to determine residues of quizalofop-P ethyl and quizalofop-P in/on the following commodities from the storage stability, crop field trial, and processing studies associated with this petition: barley grain, hay, and straw; wheat forage, grain, hay, and straw; and wheat bran, flour, germ, middlings, and shorts. Details of the method are available in 45885803.der (MRIDs 45885803 and 45885804).

The petitioner has proposed the current HPLC/UV enforcement method (DuPont Method AMR-153-83, Revision 3, see below) as a confirmatory method for the HPLC data-collection method.

A successful ILV trial was conducted using samples of wheat straw fortified with quizalofop-P ethyl and quizalofop-P at 0.05 ppm (LOQ and proposed tolerance level), 0.10 ppm, and 6.5 ppm each (MRID 45858504). No radio validation data were submitted for the method. Because the extraction procedures of the method are relatively rigorous, no radio validation data will be required to support the method.

Enforcement method: The petitioner has proposed the existing enforcement method, "Determination of Residues of DPX-Y6202, DPX-Y6202 Acid, and DPX-Y6202 Acid Conjugates in Soybeans and Soybeans Fractions" (DuPont Metbod AMR-153-83, Revision 3, January 1987; MRID 40322410; PP# 5F3252, 12/18/87, G. Otakie), for the enforcement of

tolerances for quizalofop-P ethyl residues in/on barley, flax, sunflower, and wheat commodities. This method involves extraction of samples, other than oil, with acetone and water acidified with glacial acetic acid. Oil samples are mixed with hexane, and residues are extracted into acetonitrile. The extracts are adjusted to pH 5 using base or buffer and then a mixture of β-glucosidase and cellulase enzymes is used to convert any quizalofop conjugates to quizalofop. Residues of quizalofop ethyl and quizalofop are then extracted from the aqueous phase using chloroform. Liquid chromatography is used to separate quizalofop from quizalofop ethyl, and quizalofop residues are methylated. Residues of quizalofop ethyl and quizalofop-methyl are determined by HPLC/UV. The LOQ is 0.05 ppm.

This method has been validated by ACB and submitted to FDA for publication in PAM Vol. II; however, the method was accepted for the soybean tolerance only. ACB noted that the complexity of the method may require an analyst to perform several practice runs. It was concluded that additional methodology development work would be necessary if tolerances were proposed for other crops (PP# 3F3252, 6/27/88, G. Otakie). E.I. du Pont de Nemours has since submitted a different, less complex method, referred to as LAN-1. The method involves extraction of samples with acetonitrile/1% acetic acid, hydrolysis of extracts with a mixture of cellulase and β-glucosidase, and further hydrolysis with esterase. Residues are partitioned into acetonitrile/dichloromethane, concentrated, and transferred into acetonitrile and phosphate buffer. After HPLC column cleanup, extracts are analyzed by HPLC/UV. The LOQ is 0.05 ppm (PP# 3F4268, F. Griffith, 3/30/95;).

The LAN-1 method was forwarded to ACB for PMV; ACB examined the method and identified several deficiencies which needed addressing before the PMV is finalized (D219639, 10/11/95, F. Griffith)

No validation data for the current enforcement method (AMR-153-83), or the newer method (LAN-1), have been submitted for the crop commodities proposed in the current petition.

Conclusions. The submitted residue analytical method data are tentatively adequate to satisfy data requirements. Because the petitioner did not include any validation data for barley, flax, sunflower, or wheat commodities analyzed using the current enforcement method (or newer method LAN-1), and because the extraction procedures of the data-collection methods differ significantly from the extraction procedures of the existing enforcement method, HED cannot conclude that the current enforcement method would be adequate for the enforcement of tolerances for residues in/on barley, flax, sunflower, or wheat commodities.

Sufficient data have been submitted to support the use of the data-collection methods (SARS-98-06 and Meth-147), for enforcement purposes; therefore, the methods will be forwarded to ACB for PMV. We note that the ILV laboratory recommended some changes/clarifications to HPLC Method SARS-98-06. Unless ACB concludes differently, the modifications recommended by the ILV laboratory will have to be worked into the method prior to its acceptance as a tolerance enforcement method.

We note that the method descriptions did not address the issue of determination of the S-enantiomers of quizalofop ethyl and quizalofop. Because the KOH hydrolysis step would

convert both the R- and S-enantiomers of quizalofop ethyl and quizalofop acid to the intermediate MeCHQ, all reported results for total quizalofop-P ethyl residues would include residues of both the R- and S-enantiomers of quizalofop ethyl and quizalofop acid. Both methods should be modified to include a statement addressing the inclusion of the S-enantiomers in the method determination, because the S-enantiomers are included in the tolerance expression for quizalofop-P ethyl.

860.1340 Residue Analytical Methods – Livestock Commodities

Adequate methods are available for the enforcement of tolerances in livestock commodities (PP# 3F3252, 6/27/88, G. Otakie). A HPLC/UV Method (AMR-627-86, MRID 40322403) is available for the determination of residues of quizalofop ethyl, quizalofop, and quizalofop-methyl in livestock tissues. Another HPLC/UV Method (AMR-515-86, Revision A; MRID 40322408) is available for determination of residues of quizalofop ethyl, quizalofop, and quizalofop-methyl in milk. Methods AMR-627-86 and AMR-515-86 have undergone PMV and have been forwarded to FDA for publication in PAM Volume II. In addition, HPLC/UV Methods AMR-846-87 (MRID 40322405), AMR-845-87 (MRID 40322409), and AMR-623-86 (MRID 40322404) are available for the determination of residues of quizalofop ethyl, quizalofop, and quizalofop-methyl in livestock fat, cream, and eggs, respectively. Methods AMR-846-87, AMR-845-87, and AMR-623-86 have been forwarded to FDA for publication in PAM Volume II as letter methods. The methods involve extraction of samples with acetonitrile, methanol, acidified acetone, or acidified acetone/hexane (depending on the matrix), treatment of the extract with enzymes (lipase and esterase) to disassociate the fat and to convert residues of quizalofop ethyl and quizalofop-methyl to quizalofop. Quizalofop residues are then partitioned into chloroform for analysis by HPLC/UV. Residue results are reported in terms of residues of quizalofop. The reported LOQs are 0.02 ppm for muscle and 0.05 ppm for liver, kidney, cream, and fat; based on validation data, the LOQ for egg and milk is 0.01 ppm.

860.1360 Multiresidue Methods

No multiresidue method data were submitted with the current petition; however, multiresidue method data for quizalofop ethyl have been submitted previously. According to the Pesticide Analytical Manual (PAM) Volume 1, Appendix II (FDA PESTDATA database dated 10/99), quizalofop ethyl is completely recovered using Multiresidue Methods Section 302 (Luke Method; Protocol D). The database did not contain any information pertaining to the recovery of quizalofop or quizalofop-methyl using the multiresidue methods.

Multiresidue method data for the metabolites of quizalofop-methyl and quizalofop should be submitted

860.1380 Storage Stability

The storage durations and conditions of samples from the barley, flax, sunflower, and wheat crop field trial and processing studies were submitted to support this petition (Table 4).

Table 4. Summary of Storage Conditions and Intervals of Samples from the Crop Field Trial and Processing Studies.

Matrix	Storage Temp. (°C) & Durations	Intervals of Demonstrated Storage Stability	Reference
Barley, hay	-20 ± 5 2.7-7.5 months	12.7 months for quizalofop-P ethyl and quizalofop-P in/on frozen wheat forage and grain, and 11.2 months for residues in/on frozen wheat hay and straw.	45885802.der
Barley, grain	1.5-6.7 months		
Barley, straw	1.5-7.3 months		
Flax seed	-23 to -20 1.2-1.9 months	48 and 36 months for quizalofop ethyl and quizalofop, respectively, in/on frozen soybean seed.	45089201.der 45089202.der
Sunflower, seed	≤-16 1.0-5.7 months	48 and 36 months for quizalofop ethyl and quizalofop, respectively, in/on frozen soybean seed; and 28 months for quizalofop in/on frozen cotton seed, meal, and oil.	44967701.der 44967702.der
Sunflower, meal	4.9 months		
Sunflower, oil	1.1 months		
Wheat, forage	-20 ± 5 1.7-7.2 months	12.7 months for quizalofop-P ethyl and quizalofop-P in/on frozen wheat forage and grain, and 11.2 months for residues in/on frozen wheat hay and straw.	45885801.der3 45885801.der3
Wheat, hay	1.9-6.8 months		
Wheat, grain	1.1-4.2 months		
Wheat, straw	2.2-5.6 months		
Wheat, processed commodities	≤ -12 <1.0 month	None required	45885801.der3

Storage stability data for quizalofop ethyl and quizalofop in/on various matrices, including cotton and soybean commodities, have been submitted previously. Adequate storage stability data are available for soybean seed indicating that residues of quizalofop ethyl and quizalofop are stable during up to 48 and 36 months, respectively, of frozen storage (PP# 5F3252, 12/18/87, G. Otakie). In addition, data are available indicating that residues of quizalofop are relatively stable in/on cotton seed, meal, and oil stored frozen for up to 28 months (PP# 3F42681/5H5720; D220215-17, F. Griffith, 2/13/96). Since the parent ethyl ester hydrolyzes rapidly to quizalofop after application, HED concludes that separate storage stability data for quizalofop ethyl/quizalofop-P ethyl in cotton commodities are not necessary.

In support of the wheat and barley crop field trials data submitted with this petition, Nissan Chemical Industries has submitted the results of storage stability studies with quizalofop-P ethyl and its acid metabolite quizalofop-P in wheat matrices (45885801.der3). Separate untreated samples of wheat forage, hay, grain, and straw were fortified with a standard of quizalofop-P ethyl or quizalofop-P at 2.5 ppm and placed in frozen storage at ca. -20 °C. Samples were analyzed for residues of quizalofop-P ethyl and quizalofop-P at storage durations of 0, 32-39, and 341-386 days using the HPLC method (Morse Method Meth-147). The results indicate that under these conditions, residues of quizalofop-P ethyl and quizalofop-P are stable in/on wheat forage and grain for up to 12.7 months, wheat hay for up to 11.3 months, and wheat straw for up to 11.2 months.

Conclusions. The available storage stability data are adequate to support the sample storage durations and conditions from the submitted field trials and/or processing studies on barley, flax,

sunflower, and wheat. The storage stability data for wheat commodities may be translated to support the storage durations and conditions of samples from the barley crop field trials. The storage stability data for soybean seed and cotton seed, meal, and oil may be translated to support the storage conditions and durations of samples from the flax and sunflower crop field trials and the sunflower processing study. Because samples of wheat processed commodities were stored frozen and analyzed within one month of sample collection, supporting storage stability data are not needed.

860.1400 Water, Fish, and Irrigated Crops

There are no proposed uses that are relevant to this guideline topic.

860.1460 Food Handling

There are no proposed uses that are relevant to this guideline topic.

860.1480 Meat, Milk, Poultry, and Eggs

There are several feedstuffs associated with the proposed uses of quizalofop-P ethyl: barley grain, hay, and straw; flax meal; sunflower meal; and wheat forage, grain, hay, straw, aspirated grain fractions, and milled byproducts. The maximum theoretical dietary burdens of quizalofop-P ethyl to livestock, considering both the proposed and registered uses of quizalofop-P ethyl, are presented in Table 5.

Ruminants

A dairy cattle feeding study was submitted previously (PP# F3951, 12/18/87, G. Otakie, and PP# F3951, 3/4/92, J. Stokes). In the study, three groups of three lactating dairy cows (plus a control group) were fed quizalofop ethyl ester at 0.1, 0.5, and 5.0 ppm in the diet for 28 consecutive days. These levels correspond to 0.04x, 0.19x, and 1.9x the maximum theoretical dietary burden to beef and dairy cattle calculated above. Milk was collected daily, and a sub-sample was divided into skim milk and cream. Two cows from each group were sacrificed after 28 days, and samples of fat, skeletal muscle, liver, and kidney were collected and analyzed. The remaining cow in each test group was used to measure depuration, and was sacrificed 7 days after dosing finished. The methods used for analysis converted residues of quizalofop ethyl and quizalofop-methyl to quizalofop; therefore, all reported residue results were expressed in terms of quizalofop. Quizalofop residues in whole milk, skim milk, and cream from the control, and the 0.1- and 0.5-ppm dose groups were <0.01 ppm (<0.05 ppm in cream). In samples from the 5-ppm dose group, quizalofop residues ranged 0.01-0.02 ppm in whole milk, reaching a plateau on the fourth day of dosing. Quizalofop residues were found to partition into the cream samples from this group, with residues reaching plateaus of 0.26, 0.28, and 0.31 ppm after 2, 3, and 4 weeks of dosing, respectively. Quizalofop residues were <0.02 ppm in skeletal muscle, and <0.05 ppm in liver, kidney, and fat samples from all three dose groups, with the exception of one kidney sample from the 5-ppm dose group which had quizalofop residues of 0.05 ppm.

Table 5. Calculation of Maximum Theoretical Dietary Burdens of Quizalofop-P ethyl Residues to Livestock.				
Feedstuff	% Dry Matter [1]	% Diet [1]	Recommended Tolerance (ppm)	Dietary Contribution (ppm)[2]
Beef Cattle				
Pea, field, vines	25	20	3.0	2.40
Sunflower, meal	92	15	1.9	0.31
Wheat, grain	89	20	0.05	0.01
TOTAL BURDEN				**2.70**
Dairy Cattle				
Pea, field, vines	25	20	3.0	2.40
Sunflower, meal	92	15	1.9	0.31
Wheat, grain	89	20	0.05	0.01
TOTAL BURDEN				**2.72**
Poultry				
Sunflower, meal	92	25	1.9	0.475
Wheat, grain	89	70	0.05	0.035
TOTAL BURDEN				**0.510**
Swine				
Canola, meal	88	15	1.5	0.225
Sunflower, meal	92	20	1.9	0.380
Pea, field, seed	90	20	0.25	0.050
TOTAL BURDEN				**0.655**

1. Table 1 (OPPTS Guideline 860.1000) including planned revision for 2006.
2. Contribution = ([tolerance /% DM] x % diet) for beef and dairy cattle; contribution = ([tolerance] x % diet) for poultry and swine.

Conclusion. The available feeding study data indicate that the established tolerances for combined residues of quizalofop ethyl and its metabolites quizalofop and quizalofop-methyl in the fat, meat, and meat byproducts of cattle, goat, hog, horse, and sheep at 0.05 ppm for fat and meat byproducts and 0.02 ppm for meat are adequate and do not need to be revised based on the requested uses of quizalofop-P ethyl. Based on whole milk residues being 0.02 ppm at 1.9x feeding level, the established tolerance of 0.01 ppm for milk is still adequate. A tolerance of 0.05 ppm has been established for milk fat. The available data indicate that a revised tolerance is needed; based on the maximum residues in milk of 0.02 ppm at a 1.9x dosing rate and an assumed 25x concentration factor for milk fat, expected residues at a 1x dosing rate would be 0.25 ppm; therefore, a revised milk fat tolerance of 0.25 ppm is needed.

Poultry

A poultry feeding study has been submitted and reviewed (PP# F3951, 12/18/87, G. Otakie). Three groups of 20 hens per group (plus one control group) were dosed with quizalofop ethyl at 0.1, 0.5, and 5 ppm in the diet for 28 consecutive days: each dose group was subdivided into four subsets of five birds each. These levels correspond to 0.20x, 1x, and 10x the maximum theoretical dietary burden calculated above. Eggs were collected daily. After 28 days, 15 of the hens in each test group were sacrificed, and samples of fat, liver, kidney, breast and thigh

muscles were collected and analyzed; tissues from each test group subset were pooled prior to analysis. The remaining five hens in each test group were used to measure depuration, and were sacrificed 7 days after dosing finished. The methods used for analysis converted residues of quizalofop ethyl and quizalofop-methyl to quizalofop; therefore, all reported residue results were expressed in terms of quizalofop. Quizalofop residues were <0.05 ppm in liver samples and <0.02 ppm in breast and thigh muscle samples from all dose groups, and were <0.05 ppm in kidney and fat samples from the 0.1- and 0.5-ppm dose groups. In samples from the 5-ppm dose group, quizalofop residues were 0.09 ppm in one pooled kidney sample, 0.05 and 0.06 ppm in two fat samples, and were <0.05 ppm in the other kidney and fat samples. In eggs, residues were <0.02 ppm in all samples from all dose groups with the exception of one sample from the 5-ppm dose group which had quantifiable residues at 0.02 ppm.

Conclusion. The available feeding study data indicate that the established tolerances for combined residues of quizalofop ethyl and its metabolites quizalofop and quizalofop-methyl in egg at 0.02 ppm and the fat, meat, and meat byproducts of poultry at 0.05 ppm for fat and meat byproducts and 0.02 ppm for meat are adequate and do not need to be revised based on the requested uses of quizalofop-P ethyl.

860.1500 Crop Field Trials

45885802.der (Barley)
45089201.der (Flax)
44967701.der (Sunflower)
45885801.der (Wheat)

To support the use of quizalofop-P ethyl (0.88 lb ai/gal EC formulation) on barley, flax, sunflower, and wheat, Nissan has submitted field trial data for these commodities. The results from these field trials are discussed below and summarized in Table 6. We note that all crop field trials were conducted using a DuPont quizalofop-P ethyl product (Assure II; 0.88 lb ai/gal EC; EPA Reg. No. 352-541). The petitioner has stated that their product (Targa® herbicide; EPA Reg. No. 33906-9) is identical in terms of formulation to the DuPont product.

Table 6. Summary of Residue Data from Crop Field Trials with Quizalofop-P ethyl.

Crop matrix	Total Applic. Rate (lb ai/A)	PHI (days)	Total Quizalofop-P ethyl Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median	Mean	Std. Dev.
BARLEY (proposed rate = 0.083 lb ai/A total application rate)									
Barley, hay	0.066-0.070	48-219	50	<0.05	<0.05	<0.05	<0.025	<0.025	0
Barley, grain	0.066-0.070	90-255	50	<0.05	<0.05	<0.05	<0.025	<0.025	0
Barley, straw	0.066-0.070	90-255	50	<0.05	<0.05	<0.05	<0.025	<0.025	0
FLAX (proposed rate = 0.165 lb ai/A total application rate, 70-day PHI)									
Flax, seed	0.161-0.164	70-74	8	<0.05	<0.05	<0.05	<0.025	<0.025	0
SUNFLOWER (proposed rate = 0.124 lb ai/A total application rate, 60-day PHI)									
Sunflower seed	0.120-0.124	60-61	16	0.14	1.32	1.31	0.41	0.51	0.35

Table 6. Summary of Residue Data from Crop Field Trials with Quizalofop-P ethyl.									
Crop matrix	Total Applic. Rate (lb ai/A)	PHI (days)	Total Quizalofop-P ethyl Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median	Mean	Std. Dev.
WHEAT (proposed rate = 0.083 lb ai/A total application rate)									
Wheat, forage	0.065-0.073	21-209	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, hay	0.065-0.073	55-231	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, grain	0.065-0.073	90-272	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, straw	0.065-0.073	90-272	64	<0.05	<0.05	<0.05	<0.025	<0.025	0

1 HAFT = Highest average field trial result.

Barley

Nissan Chemical Industries, Ltd. has submitted field trial data for quizalofop-P ethyl on barley. A total of twenty-five trials were conducted in the U.S. and Canada during the 2001 and 2002 growing season. The U.S. trials were conducted in Zones 1 (NY; 1 trial), 5 (KS and ND; 2 trials), 7 (NE and ND; 2 trials), 9 (UT; 1 trial), 10 (CA; 1 trial), and 11 (ID and WA; 2 trials). The Canadian trials were conducted in Zones 5 (ON; 1 trial), 5B (QC; 1 trial), 7 (SK; 1 trial), 7A (AB; 1 trial), and 14 (AB, MB, and SK; 12 trials). The number and locations of field trials are in accordance with OPPTS Guideline 860.1500; we note that the number and locations are also in accordance with Pest Management Regulatory Agency (PMRA) Directive 98-02, Section 9. All trials were conducted on spring barley, except for one which was conducted on fall barley.

At each test location, a single preplant broadcast application of a 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) was made to the soil surface at ~0.068 lb ai/A (0.8x the proposed maximum seasonal rate) on or the day before planting. All applications were made using ground equipment in spray volumes of 5.0-20.5 gal/A, with an adjuvant (petroleum-based crop oil concentrate) added to the spray mixture. Samples of barley hay were harvested 48-219 days after application and dried in the field for 1-12 days, and samples of mature barley grain and straw were harvested 90-255 days after application.

Samples of barley matrices were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using an HPLC method, Morse Method Meth-147. The method has been validated in conjunction with the barley crop field trials and is adequate for data collection. The validated LOQ was 0.05 ppm, and the defined limit of detection (LOD) was 0.017 ppm for all barley matrices. Samples were stored frozen for up to ~7.5 months from collection to analysis, a duration supported by the available storage stability data.

The results of the barley crop field trials are presented in Table 6. Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of barley hay harvested 48-219 days after application, and all samples of barley grain and straw harvested 90-255 days after application.

No residue decline study was included in the submission; these data are not required because application to barley is to be made prior to crop emergence.

Flax

The petitioner has submitted field trial data for quizalofop-P ethyl on flax seed. Four trials were conducted in Zones 5 (MN and ND; 2 trials) and 7 (ND; 2 trials) during the 1999 growing season. The number and locations of field trials are not in accordance with OPPTS Guideline 860.1500; an additional trial is recommended in Zone 7.

At each test location, two postemergence broadcast applications of a 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) were made at ~0.0806 lb ai/A/application with a 6- to 8-day RTI, for a total seasonal application rate of ~0.161 lb ai/A (~1x the proposed maximum seasonal rate). All applications were made using ground equipment in spray volumes of ~15-20 gal/A, with a non-ionic surfactant added to the spray mixture. Samples of flax seed were harvested 70-74 days after the last application.

Samples of flax seed were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using an HPLC method, Method No. SARS-98-06. The method has been validated in conjunction with the flax crop field trials and is adequate for data collection. The validated LOQ was 0.05 ppm. Samples were stored frozen for up to 1.9 months from collection to analysis, a duration supported by the available storage stability data.

The results of the flax field trials are reported in Table 6. Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of flax seed harvested 70-74 days after application.

No residue decline study was included in the submission; these data are not required because residues were nonquantifiable in/on samples collected at the proposed PHI.

Sunflower

Nissan Chemical Industries, Inc. has submitted field trial data for quizalofop-P ethyl on sunflower seed. Eight trials were conducted in Zones 5 (KS, ND, and SD; 3 trials), 7 (ND and SD; 4 trials), and 8 (TX; 1 trial) during the 1998 growing season. The number and locations of field trials are in accordance with OPPTS Guideline 860.1500 for sunflowers. An oilseed variety of sunflower was planted at all trial sites, except for the TX trial, which used a non-oilseed variety.

At each test location, two postemergence broadcast applications of a 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) were made with a 6- to 7-day RTI. The first application was made at ~0.054 lb ai/A, and the second application was made at ~0.067 lb ai/A, for a total seasonal application rate of ~0.121 lb ai/A (~1x the proposed maximum seasonal rate). All applications were made using ground equipment in spray volumes

of ~10-21 gal/A, with an adjuvant (non-ionic surfactant or petroleum oil) added to the spray mixture. Samples of mature sunflower seed were harvested 60-61 days after the last application.

Samples of sunflower seed were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using HPLC methods, Method No. XAM-38 and Method No. SARS-98-06. The methods were validated in conjunction with the sunflower field trials and are adequate for data collection. The validated LOQ was 0.05 ppm. Samples were stored frozen for up to 4.5 months from collection to analysis, a duration supported by the available storage stability data.

The results of the sunflower field trials are reported in Table 6. Residues of total quizalofop-P ethyl were 0.14-1.32 ppm in/on sunflower seed harvested 60-61 days following two postemergence broadcast applications of the 0.88 lb ai/gal EC formulation at a total rate of 0.120-0.124 lb ai/A.

No residue decline studies were included in the submission. Because the applications are made during flowering, a residue decline study is required.

Wheat

The petitioner has submitted field trial data for quizalofop-P ethyl on wheat. A total of thirty-two trials were conducted in the U.S. and Canada during the 2001 and 2002 growing season. The U.S. trials were conducted in Zones 2 (NC; 1 trial), 4 (AR; 1 trial), 5 (KS, NE, and ND; 3 trials), 6 (OK and TX; 3 trials), 7 (ND, NE, and SD; 3 trials), 8 (KS and TX; 3 trials), and 11 (ID; 1 trial). The Canadian trials were conducted in Zones 5 (ON; 2 trials), 7 (AB and SK; 2 trials), 7A (AB; 3 trials), and 14 (AB, MB, and SK; 10 trials). Nine trials were conducted on winter wheat, and the remainder were conducted on spring wheat. The number and locations of field trials are in accordance with OPPTS Guideline 860.1500; we note that the number and locations are also in accordance with PMRA Directive 98-02, Section 9.

At each test location, a single preplant broadcast application of a 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) was made to the soil surface at ~0.068 lb ai/A (0.8x the proposed maximum seasonal rate), on or the day before planting. All applications were made using ground equipment in spray volumes of 4.9-20.7 gal/A, with an adjuvant (petroleum-based crop oil concentrate) added to the spray mixture. Samples of wheat forage were harvested 21-209 days after application; samples of wheat hay were harvested 55-231 days after application and dried in the field for 1-10 days; and samples of mature wheat grain and straw were harvested 90-272 days after application.

Samples of wheat matrices were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using an HPLC method, Morse Method Meth-147. The method has been validated in conjunction with the wheat crop field trials and is adequate for data collection. The validated LOQ was 0.05 ppm, and the defined LOD was 0.017 ppm for all wheat matrices. Samples were stored frozen for up to ~7.2 months from collection to analysis, a duration supported by the available storage stability data.

The results of the wheat field trials are reported in Table 6. Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of wheat forage harvested 21-209 days after application, wheat hay harvested 55-231 days after application, and wheat grain and straw harvested 90-272 days after application.

No residue decline study or aspirated grain fractions data were included in the submission. These data are not required because application to wheat is to be made prior to crop emergence.

Conclusions. For barley and wheat, an adequate number of field trials were conducted in representative geographic regions, samples were analyzed using an adequate method, and the sample storage durations are supported by the available storage stability data. The available barley and wheat data are adequate and will support the use of a single preemergence application of quizalofop-P ethyl (0.88 lb ai/gal EC formulation) at 0.068 lb ai/A; the proposed label should be amended to reflect this use pattern. The data also support the use of a petroleum-based crop oil concentrate in the spray mix. The available data would support tolerances at the LOQ (0.05 ppm) for the following commodities: barley grain, barley hay, barley straw, wheat forage, wheat grain, wheat hay, and wheat straw.

For flax, only four crop field trials were conducted; OPPTS 860.1500 requires a total of five field trials for flax. However, because a field trial conducted at an exaggerated rate of 5x to generate samples for processing (see 860.1520 Processed Food and Feed) yielded nonquantifiable residues in/on flax seed samples, HED concludes that an additional crop field trial is not required to support the proposed use on flax. The available flax field trial data will support a maximum of two applications of quizalofop-P ethyl (0.88 lb ai/gal EC formulation) at ~0.081 lb ai/A/application for a total seasonal application rate of ~0.161 lb ai/A. The data support a 7-day RTI, a 70-day PHI, and the use of a non-ionic surfactant in the spray mix. The data will support a tolerance at the LOQ (0.05 ppm) for flax seed.

For sunflower, an adequate number of field trials were conducted in representative geographic regions; however, no residue decline data were included in the submission. Because application may be made when the plant is flowering and residues were readily quantifiable in harvested samples, a residue decline study should be submitted for sunflower. In the study, samples should be collected at 3 to 5 sampling times in addition to the requested PHI; the sampling times should all fall within the crop stage when harvesting could reasonably be expected to occur, should be approximately equally spaced and, where possible, should represent both shorter and longer PHIs than that requested.

The available sunflower data support the use of a maximum of two applications of quizalofop-P ethyl (0.88 lb ai/gal EC formulation) at ~0.054 lb ai/A and ~0.067 lb ai/A, for a total seasonal application rate of ~0.121 lb ai/A. The data support a 7-day RTI, a 60-day PHI, and the use of an adjuvant (non-ionic surfactant or petroleum oil) added to the spray mix. The data will support a tolerance of 1.9 ppm for sunflower seed.

860.1520 Processed Food and Feed

45089202.der (Flax)
44967702.der (Sunflower)
45885801.der2 (Wheat)

Flax

Nissan submitted a processing study with flax seed. In one trial conducted in MN, flax seed was harvested 74 days following a single postemergence broadcast application of the 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) at 0.323 lb ai/A (2x the proposed maximum seasonal rate) or 0.810 lb ai/A (5x). Flax seed treated at the highest application rate was chosen for the processing study. Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on flax seed treated at the exaggerated rate (5x the field trial application rate); therefore, RAC samples were not processed into meal.

Samples of flax seed were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using an HPLC method, Method No. SARS-98-06. The method has been validated in conjunction with flax crop field trials and the processing study and is adequate for data collection. The validated LOQ was 0.05 ppm. Samples were stored frozen for up to 1.2 months from collection to analysis, a duration supported by the available storage stability data.

Sunflower

Nissan submitted a processing study with sunflower seed. In one trial conducted in ND in 1998, sunflower seed was harvested 60 days following a single postemergence broadcast application of the 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) made at 0.121, 0.362, or 0.604 lb ai/A (1x, 2x, and 5x the proposed maximum seasonal rate, respectively). Sunflower seed treated at the highest application rate (5x) was chosen for the processing study. Sunflower seed was processed into meal and oil using simulated commercial processing procedures.

Samples of sunflower seed, meal, and oil were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using HPLC methods; Method No. XAM-38 was used for the analysis of oil samples and Method No. SARS-98-06 was used for the analysis of seed and meal samples. The two methods are essentially the same, and were adequate for data collection based on acceptable concurrent method recovery data. The validated LOQ was 0.05 ppm for all matrices. Samples of seed, meal, and oil were stored frozen for up to 5.7 months, 4.9 months, and 1.1 months, respectively, from collection to analysis; these durations are supported by the available storage stability data.

Residues of total quizalofop-P ethyl were 2.45 ppm in/on sunflower seeds treated at 5x. The processing data for meal and oil indicate that residues of total quizalofop-P ethyl may concentrate slightly in meal (1.2x average processing factor) but do not appear to concentrate in sunflower oil (<0.1x average processing factor).

The reported processing factors do not exceed the theoretical concentration factors for sunflower, 4.5x for meal and 2.5x for oil (Tables 2 and 3 of OPPTS Guideline No. 860.1520).

Wheat

Nissan has submitted a processing study with wheat. In one trial conducted in ID, wheat grain was harvested 110 days following a single preplant broadcast application of the 0.88 lb ai/gal EC formulation of quizalofop-P ethyl (Assure II; EPA Reg. No. 352-541) at 0.35 lb ai/A (5x the proposed maximum seasonal rate). Bulk treated and untreated wheat grain samples were processed into bran, flour, germ, middlings, and shorts using simulated commercial processing procedures.

Samples of wheat grain and its processed commodities (bran, flour, germ, middlings, and shorts) were analyzed for residues of total quizalofop-P ethyl (quizalofop-P ethyl, quizalofop-P, and the S-enantiomers of these compounds) using an HPLC method, Morse Method Meth-147. The method has been validated in conjunction with the wheat processing study and is adequate for data collection. The validated LOQ was 0.05 ppm for wheat grain and its processed commodities, and the defined LOD was 0.017 ppm for all wheat matrices. Samples of grain were stored frozen for up to 1.7 months from collection to analysis, a duration supported by the available storage stability data. Wheat processed commodities were stored frozen and analyzed within 27 days of collection; therefore, supporting storage stability data are not required.

Residues of total quizalofop-P ethyl were less than the method LOQ (<0.05 ppm) in/on wheat grain. Residues of total quizalofop-P ethyl were also less than the method LOQ in processed wheat bran, flour, germ, middlings, and shorts. Processing factors were not calculated.

Conclusions. The submitted processing data are adequate to satisfy data requirements. The data for wheat processed commodities may be translated to barley processed commodities. The processing data indicate that tolerances are not needed for the processed commodities of barley, flax, and wheat, or for sunflower oil.

The sunflower processing data indicate that total quizalofop-P ethyl residues concentrate in sunflower meal. Based on the average processing factor, 1.2x, and the HAFT for sunflower seed, 1.31 ppm, expected residues in sunflower meal following treatment at 1x would be 1.6 ppm. Because the expected residues are less than the recommended tolerance for sunflower seed, 1.9 ppm, a tolerance for sunflower meal is not needed.

860.1650 Submittal of Analytical Reference Standards

Analytical standards for quizalofop-P ethyl and metabolites quizalofop and quizalofop-P-methyl are currently available in the National Pesticide Standards Repository (personal communication with Dallas Wright, ACB, 2/16/06).

860.1850 Confined Accumulation in Rotational Crops

Adequate confined rotational crop studies were submitted previously. In the studies, rotational crops of red beets, lettuce, wheat, peanuts, and cotton were planted 30 and 62 days following treatment of the soil with [phenyl-^{14}C]quizalofop ethyl and [quinoxaline-^{14}C]quizalofop ethyl. Over 50% of the residues in rotational crops were characterized and identified; the studies indicate that the metabolic pathway in rotational crops is the same as for primary crops. Total quizalofop residues were 0.032-0.104 ppm in rotational crop commodities from the 30-day PBI and 0.045-0.071 ppm in rotational crop commodities from the 62-day PBI . HED concluded that a 120-day PBI is needed for quizalofop-P ethyl (D219672 and D222000; 1/26/96, F. Griffith).

860.1900 Field Accumulation in Rotational Crops

Because the proposed label includes a 120-day PBI , no field rotational crop studies are needed.

860.1550 Proposed Tolerances

The Agency has previously determined that the ROC in plant commodities are quizalofop-P ethyl, its acid metabolite quizalofop-P, and the S-enantiomers of both compounds, each expressed as quizalofop-P ethyl. The ROC in livestock commodities are quizalofop ethyl, quizalofop-methyl, and quizalofop, expressed as quizalofop.

No Codex MRLs have been established for residues of quizalofop ethyl. Canadian MRLs have been established for residues of quizalofop ethyl and quizalofop in/on several commodities; flax is the only crop included in the subject petition with a Canadian MRL, at 0.05 ppm. No Mexican MRLs have been established for any of the requested crops. An International Residue Limit status sheet is attached.

A summary of the recommended tolerances from the current petition is presented in Table 7. In the acceptable barley, flax, and wheat field trials conducted at 1x the maximum proposed rate (or 1x the rate the petitioner wishes to support), total quizalofop-P ethyl residues (quizalofop-P ethyl, its acid metabolite quizalofop-P, and the S-enantiomers of both compounds) were below the LOQ (<0.05 ppm) in/on all samples. These data indicate that the proposed tolerance of 0.05 ppm for flax seed is adequate. The petitioner has proposed tolerances in/on "barley" and "wheat" at 0.05 ppm; separate tolerances in/on barley grain, barley hay, barley straw, wheat forage, wheat grain, wheat hay, and wheat straw should be proposed, each at 0.05 ppm.

Quantifiable total quizalofop-P ethyl residues were observed in/on all samples of sunflower seed; therefore, the tolerance spreadsheet was used to determine the appropriate tolerance level. Based on the calculations in the tolerance spreadsheet (Appendix I, Figure I-2), the appropriate tolerance level for sunflower seed is 1.9 ppm, slightly less than the proposed tolerance of 2.0 ppm.

The submitted processing study data indicate that tolerances are not needed for the processed commodities of barley, flax, and wheat, or for sunflower oil. Total quizalofop-P ethyl residues were found to concentrate in sunflower meal, with an average processing factor of 1.2x. The

HAFT residues for sunflower seed were 1.31 ppm. Therefore, the maximum expected residues in sunflower meal would be 1.6 ppm. This value is less than the recommended tolerance for sunflower seed and therefore, a separate tolerance is not needed or sunflower meal.

The proposed tolerances should be revised to reflect the correct commodity definitions as specified in Table 7.

Based on results from the available cattle feeding study and a calculated 1x MTDB of 2.72 ppm for dairy cattle, the established tolerances for combined residues of quizalofop ethyl and its metabolites quizalofop and quizalofop-methyl in the fat, meat, and meat byproducts of cattle, goat, hog, horse, and sheep at 0.05 ppm for fat and meat byproducts and 0.02 ppm for meat are adequate and do not need to be revised based on the requested uses. The established tolerance of 0.01 ppm for milk is also adequate. A tolerance of 0.05 ppm has been established for milk fat. The available data indicate that a revised tolerance is needed; based on the maximum residues in milk of 0.02 ppm at a 2x dosing rate and an assumed 25x concentration factor for milk fat, expected residues at a 1x dosing rate would be 0.25 ppm; therefore, a revised milk fat tolerance of 0.25 ppm is needed.

We note that the current tolerance expression for livestock commodities, specified in 40 CFR §180.441(a)(2) is for the combined residues of quizalofop, quizalofop ethyl, and quizalofop-methyl, all expressed as quizalofop ethyl. Because the methods used for analysis of livestock commodities reported results in terms of quizalofop and not in terms of quizalofop ethyl, the tolerance expression should be revised to specify:

"Tolerances are established for the combined residues of the herbicide quizalofop (2-[4-(6-chloroquinoxalin-2-yl-oxy)phenoxy]propanoic acid), quizalofop ethyl (ethyl-2-[4-(6-chloroquinoxalin-2-yl-oxy)phenoxy]propanoate), and quizalofop-methyl (methyl 2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propanoate), all expressed as quizalofop, as follows:"

Table 7. Tolerance Summary for Quizalofop-P ethyl.			
Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments and *Correct Commodity Definition*
Barley	0.05		Separate tolerances are needed for the following commodities:
		0.05	*Barley, grain*
		0.05	*Barley, hay*
		0.05	*Barley, straw*
Flax seeds	0.05	0.05	*Flax, seed*
Sunflower, seeds	2.0	1.9	*Sunflower, seed*
Wheat	0.05		Separate tolerances are needed for the following commodities:
		0.05	*Wheat, forage*
		0.05	*Wheat, grain*
		0.05	*Wheat, hay*
		0.05	*Wheat, straw*
Milk, fat	0.05 (established)	0.25	Increased tolerance is needed to support increased dietary burden.

References

CB No.: 1127
Subject: PP# 5F3252 [RCB # 1127]. DPX-Y6202 (Assure®) Herbicide on Cotton and Soybeans. Evaluation of Analytical Methodology and Residue Data (Accession Nos. 073529 and 073547).
From: M. Firestone
To: R. Taylor and Toxicology Branch
Date: 9/25/85
MRIDs: [Accession Nos. 073529 and 073547]

CB Nos.: 2806, 2806, 2810, and 2811
Subject: PP# 5F3252/FOP # 6H5479 Quizalofop ethyl (Assure®) on Soybeans. Amendment Dated August 31, 1987
From: G. Otakie
To: R. Taylor and Toxicology Branch
Date: 12/18/87
MRIDs: 40322401-40322413, 40336201, and 40337101

CB No.:	None
Subject:	PP# 3F3252/FAP # 6H5479 Ethyl 2-[4-(6-chloroquinoxalin-2-yl oxy)phenoxy] Propanoate (Quizalofop ethyl) on Soybeans, Liver, and Milk - Results from EPA Method Validation Dated May 25, 1988
From:	G. Otakie
To:	R. Taylor
Date:	6/27/88
MRIDs:	None
CB Nos.:	5852 & 5853
Subject:	Quizalofop-P ethyl [D+ isomer]/Assure® II: DuPont registration proposal (I.D. Nos. 352-LUE and 352-LUR; Record Nos. 250157 and 250158)
From:	W. Hazel
To:	R. Taylor
Date:	3/29/90
MRIDs:	41224001 & 41206101-41206103
DP Barcodes:	D160972 & D166083
Subject:	PP# 1F3951. Quizalofop ethyl ester in/on cottonseed. Evaluation of Analytical Method and Residue Data. CBTS #'s 7640, 7641, 8229.
From:	J. Stokes
To:	R. Taylor and Toxicology Branch
Date:	3/4/92
MRIDs:	41735401-41735403 & 41919801
DP Barcode:	D182751
Subject:	Quizalofop-P ethyl ester. Comparison of the Metabolism of DPX-79376, the R Enantiomer, Optically Active Ingredient, and DPX-Y6202, the Racemic Mixture, in Soybeans. CB# 10606.
From:	J. Stokes
To:	R. Taylor
Date:	7/15/93
MRID:	42643201

DP Barcodes:	D196041, D196043, D205430, D205432, D206201, D206200, & D212620-D212622
Subject:	PP # 3F4268 - Quizalofop-P ethyl Ester (Assure® II) On The Legume Vegetables (Succulent Or Dried) And Foliage Of Legume Vegetables Crop Groups, Sugar beet Tops, Roots, Molasses, and Cottonseed. Review of Magnitude of the Residue Data and Residue Analytical Method and the February 22, 1995, Amendment. [CBTS #s 12699, 12700, 14060, 14061, 14148, 14149, and 15196-98]
From:	F. Griffith
To:	R. Taylor and J. Smith
Date:	3/30/95
MRIDs:	42827501-42827509, 43314001, & 42439101
DP Barcode:	D219639
Subject:	PP # 3F4268 - Quizalofop-P ethyl ester (Assure® II) on Legume Vegetables (Succulent or Dried) and Foliage of Legume Vegetables Crop Group, Sugar beet Tops, Roots, and Molasses, and Cottonseed. Evaluation of the Analytical Chemistry Laboratory Prereview of the Tolerance Method Validations for Quizalofop-P ethyl Ester. [CBTS # 16260]
From:	F. Griffith
To:	R. Taylor and D. Marlow
Dated:	10/11/95
MRIDs:	43314001 and 42927509
DP Barcode:	D219672 and D222000
Subject:	PP # 5E4590 - Quizalofop-P ethyl ester (Assure® II) on Pineapples. Review of Magnitude of the Residue Data and Residue Analytical Method. [CBTS # 16279 and 16681].
From:	F. Griffith
To:	H. Jamerson and K. Whitby
Dated:	1/26/96
MRIDs:	43782501
DP Barcodes:	D220215, D220216, and D220217
Subject:	PP # 3F4268/5H5720 - Quizalofop-P ethyl ester (Assure® II) on the Legume Vegetables (Succulent or Dried) and Foliage of Legume Vegetables Crop Groups, Sugar beet Tops, Roots, Molasses, and Cottonseed. Review of the July 27, Sept., 22 and 26, 1995, Amendments. [CBTS #s 16400, 16401, and 16402].
From:	F. Griffith
To:	R. Taylor and K. Whitby
Dated:	2/13/96
MRID:	43804101

DP Barcodes:	DP Barcode D220476, D220478, and D220480
Subject:	PP # 5F4545/FAP # 6H5737 - Quizalofop-P ethyl Ester (Assure® II) on the Foliage Of Legume Vegetables (Except Soybeans) Crop Group, Canola And Canola Processed Commodities. Review of Magnitude of the Residue Data and Residue Analytical Method. [CBTS #s 16392, 16393, and 16394]
From:	F. Griffith
To:	R. Taylor and K. Whitby
Date:	2/21/96
MRIDs:	43695701 and 43695702

DP Barcode:	DP Barcode D310869
Subject:	44967701.der: Quizalofop-P ethyl: Crop Field Trial – Sunflower.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	44967701

DP Barcode:	DP Barcode D310869
Subject:	44967702.der: Quizalofop-P ethyl: Processed Food and Feed – Sunflower.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	44967702

DP Barcode:	DP Barcode D310869
Subject:	44967703.der: Quizalofop-P ethyl: Residue Analytical Method – Sunflower Seed, Meal and Oil.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	44967703 and 44967704

DP Barcode:	DP Barcode D310869
Subject:	45089201.der: Quizalofop-P ethyl: Crop Field Trial – Flax.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45089201

DP Barcode:	DP Barcode D310869
Subject:	45089202.der: Quizalofop-P ethyl: Processed Food and Feed – Flax.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45089202

DP Barcode:	DP Barcode D310869
Subject:	45885801.der1: Quizalofop-P ethyl: Crop Field Trial – Wheat.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45885801

DP Barcode:	DP Barcode D310869
Subject:	45885801.der2: Quizalofop-P ethyl: Processed Food and Feed – Wheat.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45885801

DP Barcode:	DP Barcode D310869
Subject:	45885801.der3: Quizalofop-P ethyl: Storage Stability – Wheat Commodities.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45885801

DP Barcode:	DP Barcode D310869
Subject:	45885802.der: Quizalofop-P ethyl: Crop Field Trials – Barley.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45885802

DP Barcode:	DP Barcode D310869
Subject:	45885803.der: Quizalofop-P ethyl: Residue Analytical Method –Alfalfa, Barley, and Wheat Commodities.
From:	S. Oonnithan
Date:	6/13/06
MRIDs:	45885803 and 45885804

MRIDs submitted with this petition, but not reviewed:

44967705 - Quizalofop-P ethyl FQPA Supplemental Information Document:, (Pursuant to PR Notice 97.1), November 4, 1999, 23 pp.

45089203 - Quizalofop-P ethyl FQPA Supplemental Information Document:, (Pursuant to PR Notice 97.1), April 5, 2000, 22 pp.

Attachments
International Residue Limit Status sheet
Appendix I - Tolerance Assessment Calculations

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name: ethyl(R)-(2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy)-propanoate	Common Name: Quizalofop-P ethyl	X Proposed tolerance 9 Reevaluated tolerance 9 Other	Date: 02/16/06

Codex Status (Maximum Residue Limits)	U. S. Tolerances
X No Codex proposal step 6 or above 9 No Codex proposal step 6 or above for the crops requested	Petition Number: PP# 0F6076 DP Barcode: D310869 Other Identifier: Decision 210762
Residue definition (step 8/CXL): N/A	Reviewer/Branch: RAB2/ C. Swartz
	Residue definition: quizalofop-P ethyl ester and its acid metabolite quizalofop-P and the S-enantiomers of both the ester and the acid, all expressed as quizalofop-P ethyl ester

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Barley	0.05
		Flax seeds	0.05
		Sunflower, seeds	2.0
		Wheat	0.05

Limits for Canada	Limits for Mexico
9 No Limits 9 No Limits for the crops requested	9 No Limits X No Limits for the crops requested
Residue definition: ethyl (RS) 2-[4-(6-chloroquinoxalin-2-yloxy) phenoxy] propionate, including the acid metabolites of (RS)2-[4-(6-chloroquinoxalin-2-yloxy) phenoxy]propanoic acid, all expressed as quizalofop ethyl [MRLs for the requested crops only]	Residue definition: quizalofop-P ethyl

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)
Flax	0.05		

Notes/Special Instructions:
S Funk, 02/17/2006.

Appendix I. Tolerance Assessment Calculations.

The dataset used to establish a tolerance for quizalofop-P ethyl on sunflower seed consisted of field trial data representing application rates of 0.121 lb ai/A (two applications at 0.054 and 0.067 lb ai/A) with a 60-day PHI. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs are within 25% of the maximum label application rate and minimum label PHI, respectively. The residues values used to calculate the tolerance are provided in Table I-1. Residue values represent combined residues of quizalofop-P ethyl, quizalofop-P, and the S enantiomers of quizalofop ethyl and quizalofop. All 16 field trial sample results were above the LOQ.

The quizalofop-P ethyl-sunflower seed dataset was entered into the tolerance spreadsheet. Visual inspection of the lognormal probability plot (Figure I-1) provided in the spreadsheet indicates that the dataset is reasonably lognormal. The result from the approximate Shapiro-Francia test statistic (Figure I-2) confirmed that the assumption of log-normality should not be rejected.

Since the field trial data for quizalofop-P ethyl on sunflower seed represent a large dataset (i.e., more than 15 samples) and are reasonably lognormal, the minimum of the 95% upper confidence limit (UCL) on the 95th percentile and the point estimate of the 99th percentile should be selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the 95% UCL on the 95th percentile rounds to the value 1.9 ppm and the point estimate of the 99th percentile rounds to the value 2.5 ppm (Figure I-2). Because the 1.9-ppm value was the minimum value, 1.9 ppm is the recommended tolerance level for quizalofop-P ethyl on sunflower seed.

Table I-1. Residue data used to calculate tolerance for quizalofop-P ethyl in/on sunflower seed.	
Crop	Total Quizalofop-P ethyl Residues ((total of R and S enantiomers of quizalofop ethyl and quizalofop; ppm)
Sunflower seed	0.550
	0.640
	0.350
	0.530
	0.230
	0.250
	0.600
	0.610
	0.340
	0.430
	0.370
	0.380
	0.140
	0.150
	1.300
	1.320
Regulator:	EPA
Chemical:	Quizalofop-P ethyl
Crop:	Sunflower seed
PHI:	60 days
App. Rate:	0.121 lb ai/A
Submitter:	Nissan Chemical Industries, Ltd.
MRID Citation:	MRID 44967701

Figure I-1. Lognormal probability plot of quizalofop-P ethyl field trial data for sunflower seed.

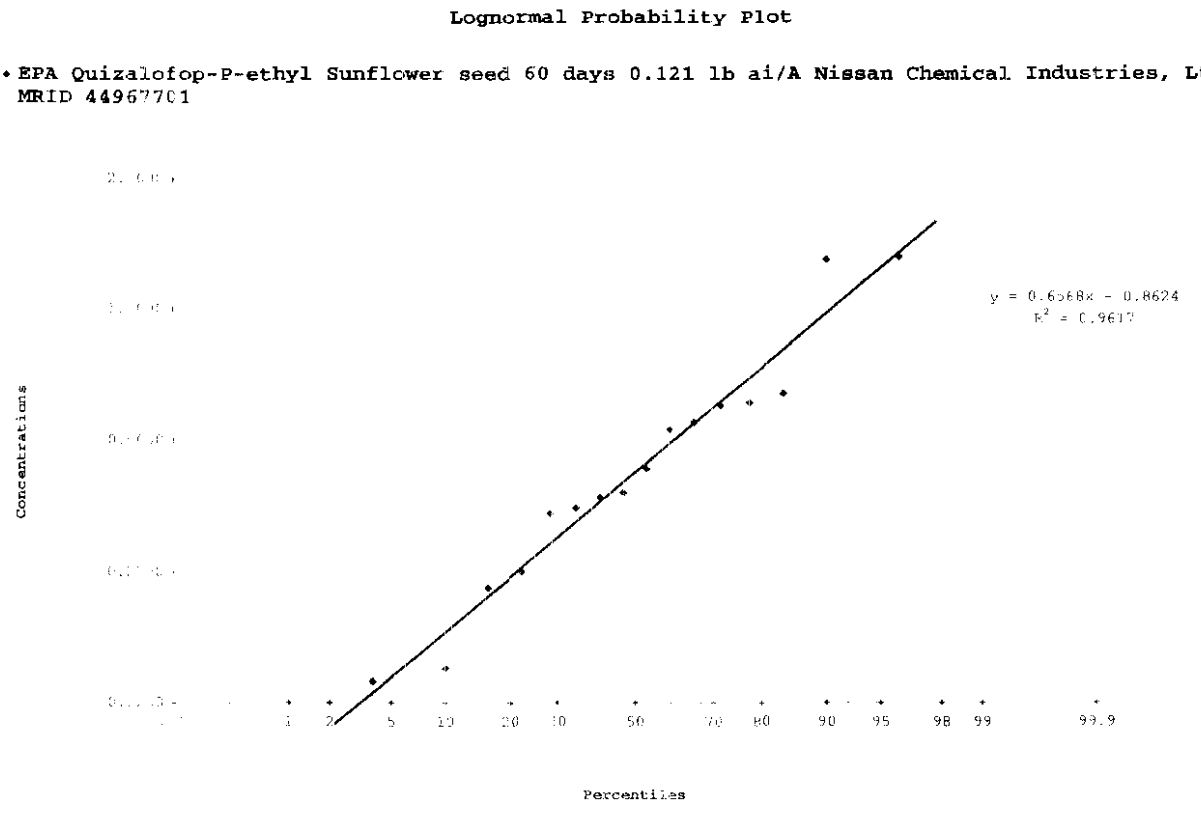


Figure I-2. Tolerance spreadsheet summary of quizalofop-P ethyl field trial data for sunflower seed.

	Regulator: EPA		
	Chemical: Quizalofop-P-ethyl		
	Crop: Sunflower seed		
	PHI: 60 days		
	App. Rate: 0.121 lb ai/A		
	Submitter: Chemical Industries, Ltd.		
	MRID Citation: MRID 44967701		
	n: 16		
	min: 0.14		
	max: 1.32		
	median: 0.41		
	average: 0.51		
	95th Percentile	**99th Percentile**	**99.9th Percentile**
EU Method I Normal	1.1 (1.4)	1.4 (1.8)	1.6 (--)
EU Method I Log Normal	1.3 (2.5)	1.9 (4.0)	3.5 (--)
EU Method II Distribution-Free	1.3		
California Method $\mu + 3\sigma$	**1.6**		
UPLMedian95th	**3.0**		
Approximate Shapiro-Francia Normality Test	0.9617 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.2.1, 7.2.2, and 7.2.3/OPPTS 860.1340/OECD IIA 4.2.5, 4.2.6 and 4.3
Residue Analytical Method –Sunflower Seed, Meal, and Oil

Primary Evaluator	S. Oonnithan, Biologist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006
Peer Reviewer	William Drew, Environmental Scientist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORTS

44967703 Hofen, J.; Keller, G. (1999) Analytical Method for the Determination of Residues of Quizalofop-P-Ethyl and Quizalofop-P in Sunflower Seed, Meal and Oil: Lab Project Number: SARS-98-06. Unpublished study prepared by Stewart Agricultural Research Services, Inc. 43 p.

44967704 Debeve, W.; Jablonski, J. (1999) Independent Laboratory Validation of the Method for the Determination of Quizalofop-P-Ethyl and Quizalofop-P in Sunflower Seeds: Lab Project Number: 007840-1; SARS-98-06; 007840-0. Unpublished study prepared by Ricerca, Inc. 125 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted a analytical method description and validation data for a data collection method, Method No. SARS-98-06, for the determination of residues of quizalofop-P-ethyl and its acid metabolite quizalofop-P in flax seed, sunflower seed, and sunflower processed commodities (meal and oil). This method, or an earlier version (Method No. XAM-38), was used to determine residues of quizalofop-P-ethyl and quizalofop-P in/on samples of flax seed, sunflower seed, and sunflower processed commodities from the crop field trial and processing studies associated with the submission D310869.

In this method, the samples are refluxed with methanolic potassium hydroxide (KOH) to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution is acidified and partitioned with hexane to extract the MeCHQ, and the hexane fraction is cleaned up by gel permeation chromatography (GPC). The extract is concentrated and redissolved in hexane for high performance liquid chromatography (HPLC) analysis with fluorescence detection. Results are converted to quizalofop-P-ethyl or quizalofop-P equivalents using a molecular weight conversion factor. We note that results are only converted to quizalofop-P equivalents for the purposes of calculating recovery in samples fortified with

quizalofop-P. The validated limit of quantitation (LOQ) reported in the method is 0.05 ppm for all matrices.

Method validation data for HPLC Method No. SARS-98-06 demonstrated adequate method recoveries of quizalofop-P-ethyl and quizalofop-P from sunflower seed, meal, and oil. Following fortification of samples with each analyte at 0.05, 0.5, and 5.0 ppm, recoveries of quizalofop-P-ethyl and quizalofop-P averaged 79% and 87%, respectively, from sunflower seed, and 74% and 87%, respectively, from sunflower meal. Recoveries of quizalofop-P-ethyl and quizalofop-P averaged 89% and 88%, respectively, from sunflower oil samples fortified with each analyte at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for flax seed. Method validation data were included with the flax seed crop field trial study submitted in conjunction with D310869; adequate recoveries of quizalofop-P-ethyl and quizalofop-P were obtained from flax seed fortified with each analyte at 0.05 and 5.0 ppm. The method validation data are sufficiently representative of the expected residue levels for the flax and sunflower commodities included in the petition associated with D310869.

The petitioner has proposed the current HPLC/UV enforcement method (Dupont Method AMR-153-83, Revision 3, January 1987; MRID 40322410) as a confirmatory method for the HPLC data-collection method.

A successful independent laboratory validation (ILV) trial was conducted using samples of sunflower seed fortified with quizalofop-P-ethyl and quizalofop-P at 0.05 and 2.0 ppm each. The ILV laboratory recommended some minor changes to the method to improve clarity; it does not appear that the method has been modified to incorporate these recommendations.

No radiovalidation data were submitted for the method. Because the extraction procedures of the method are relatively rigorous, no radiovalidation data will be required to support the method.

We note that the method description did not address the issue of determination of the S enantiomers of quizalofop-ethyl and quizalofop. Because the KOH hydrolysis step would convert both the R and S enantiomers of quizalofop-ethyl and quizalofop to MeCHQ, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the analytical method test data are tentatively classified as scientifically acceptable. HPLC Method No. SARS-98-06 should be modified to incorporate the changes recommended by the ILV laboratory to improve the clarity of the method.

The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document, D310869.

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

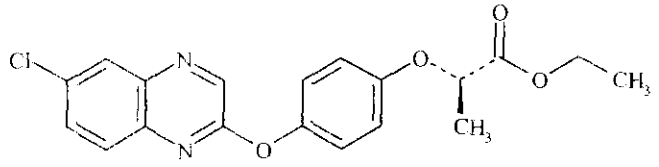
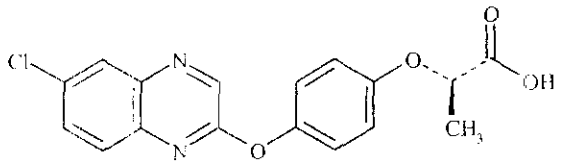
TABLE A.1. Test Compound Nomenclature.	
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)
Chemical structure	
Common name	Quizalofop-P
Company experimental name	Not provided
IUPAC name	(R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propionic acid
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid
CAS registry number	94051-08-8
End-use product (EP)	Not applicable

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.		
Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

A method description and validation data have been submitted for a data-gathering method, HPLC Method No. SARS-98-06, used to determine quizalofop-P-ethyl and quizalofop-P residues in flax seed, sunflower seed, and sunflower processed commodities (meal and oil). The HPLC method is entitled "Analytical Method for the Determination of Residues of Quizalofop-P-Ethyl and Quizalofop-P in Sunflower Seed, Meal and Oil."

This method is a modification of an HPLC method developed by Xenos Laboratories (Method No. XAM-38) and it differs from the Xenos method in the amounts of reagents and solvents used for extraction and the amount of eluate collected in the column cleanup. These modifications were made to allow for determination of a larger range of concentrations of the analyte in samples of sunflower seed and meal. Both these HPLC Methods (No. XAM-38 and SARS-98-06) were used to determine residues of quizalofop-P-ethyl and quizalofop-P in/on the sunflower seed and flaxseed crop field trials; and sunflower meal and oil from the sunflower processing study associated with D310869.

B.1.1. Principle of the Method:

Briefly, the samples are refluxed with methanolic KOH to convert quizalofop-P-ethyl and quizalofop-P residues to MeCHQ (see the structure below). The solution is acidified and partitioned with hexane to extract the MeCHQ, and the hexane fraction is cleaned up by GPC. The extract is concentrated and redissolved in hexane for HPLC analysis with fluorescence detection. Results are converted to quizalofop-P-ethyl or quizalofop-P equivalents using a molecular weight conversion factor. We note that results would only be converted to quizalofop-P equivalents for the purposes of calculating recovery in samples fortified with quizalofop-P. A summary of the Method No. SARS-98-06 is provided in Table B.1.1.

Structure of MeCHQ:

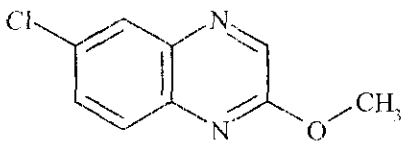


TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Sunflower Seed, Meal, and Oil.	
Method ID	SARS-98-06
Analytes	Quizalofop-P-ethyl, quizalofop-P, and the S enantiomers
Extraction solvent/technique	Homogenized samples are refluxed in 1 N methanolic KOH for 1.5 h. Water and saturated sodium chloride solution are added, and the mixture is acidified to pH 2.0 using concentrated hydrochloric acid. The extract is partitioned with hexane (2x), and the hexane phase is dried with sodium sulfate and then concentrated to near dryness after the addition of 2% diethylene glycol in acetone. The residues are redissolved in cyclohexane:ethyl acetate (85:15, v:v).
Cleanup strategies	The extract is cleaned up by GPC, using cyclohexane:ethyl acetate (85:15, v:v) to elute residues. The eluate is evaporated to dryness, after the addition of 2% diethylene glycol in acetone, and redissolved in hexane.
Instrument/Detector	HPLC with fluorescence detection, using a silica column and a mobile phase of methylene chloride:hexane (80:20, v:v). The fluorescence detector uses an excitation setting of 338 nm and an emission setting of 374 nm.
Standardization method	External standardization, using calibration standards of MeCHQ to generate a standard curve through linear regression. Results are converted to quizalofop-P-ethyl or quizalofop-P equivalents using molecular weight conversion factors.
Stability of std solutions	Stock solutions of quizalofop-P-ethyl, quizalofop-P, and MeCHQ are to be stored in amber bottles at <-15 °C and to be prepared fresh every 3 months (MeCHQ) or 6 months (quizalofop-P-ethyl and quizalofop-P). Fortification and calibration solutions are to be stored at <5 °C and prepared fresh every month.
Retention times	14 minutes

B.2. Enforcement Method

The petitioner has not proposed the submitted data-collection method for enforcement purposes.

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

The characteristics of the data-gathering method is summarized in Table C.1.2.

TABLE C.1.1. Recovery Results from Method Validation of Sunflower Seed and Sunflower Processed Commodities using the Data-Gathering Analytical Method. [1]

Matrix	Analyte	Spiking Level (ppm) [2]	Recoveries Obtained (%)	Recovery (%)		
				Mean	SD[3]	CV[4]
Sunflower seed	Quizalofop-P-ethyl	0.05	74, 76, 82	79	5	6
		0.5	73, 74, 81			
		5	80, 84, 86			
	Quizalofop-P	0.05	70, 90, 100	87	8	9
		0.5	86, 89, 91			
		5	83, 86, 88			
Sunflower meal	Quizalofop-P-ethyl	0.05	66, 72, 74	74	4	6
		0.5	73, 75, 78			
		5	73, 74, 81			
	Quizalofop-P	0.05	84, 102, 114	87	13	15
		0.5	76, 76, 77			
		5	83, 84, 87			

TABLE C.1.1. Recovery Results from Method Validation of Sunflower Seed and Sunflower Processed Commodities using the Data-Gathering Analytical Method. [1]

Matrix	Analyte	Spiking Level (ppm) [2]	Recoveries Obtained (%)	Recovery (%)		
				Mean	SD[3]	CV[4]
Sunflower oil	Quizalofop-P-ethyl	0.05	80, 82, 98	89	10	11
		0.5	81, 92, 103			
	Quizalofop-P	0.05	82, 92, 98	88	7	8
		0.5	78, 89, 90			

[1] Standards were prepared in acetonitrile for quizalofop-P-ethyl solutions and in 0.2 % acetic acid in acetonitrile for quizalofop-P solutions.

[2] Samples fortified at the 0.05- and 0.5-ppm level were analyzed using the procedures of Method No. XAM-38 (i.e., using smaller volumes of solvents and reagents and a smaller GPC eluate fraction). Samples fortified at the 5 ppm level were analyzed using the procedures of SARS-98-06.

[3] Standard deviation

[4] Coefficient of variation

The method validation recoveries of quizalofop-P-ethyl and quizalofop-P using HPLC Method No. SARS-98-06 were adequate from fortified samples of sunflower seed, meal, and oil (Table C.1.1). Following fortification of samples with each analyte at 0.05, 0.5, and 5.0 ppm, recoveries of quizalofop-P-ethyl and quizalofop-P averaged 79% and 87%, respectively, from sunflower seed, and 74% and 87%, respectively, from sunflower meal. Recoveries of quizalofop-P-ethyl and quizalofop-P averaged 89% and 88%, respectively, from sunflower oil samples fortified with each analyte at 0.05 and 0.5 ppm. Low recovery of quizalofop-P-ethyl at 66% was observed from one sunflower meal sample fortified at 0.05 ppm. We note that samples fortified at the 0.05- and 0.5-ppm level were analyzed using the procedures of Method No. XAM-38 (i.e., using smaller volumes of solvents and reagents, and a smaller GPC eluate fraction).

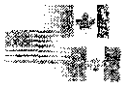


TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Sunflower Seed, Meal, and Oil.	
Analytes	Quizalofop-P-ethyl, quizalofop-P, and the S enantiomers
Equipment ID	Shimadzu HPLC system with Shimadzu RF-551 Fluorescence HPLC monitor; Phenomenex Maxsil 5 Silica column (250 x 4.6 mm); Alltech Adsorbosil silica guard column (5µ)
Limit of quantitation (LOQ)	0.05 ppm for sunflower seeds meal and oil (determined as lowest fortification level with adequate recovery)
Limit of detection (LOD)	The LOD was reported as 0.45 ng (lowest standard with a response at least 3x background); based on the calculation included in the submission, the reported value corresponds to ~0.02 ppm.
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision at 0.05, 0.5, and 5.0 ppm for sunflower seed and meal, and 0.05 and 0.50 ppm for sunflower oil. Recovery ranges (and CVs) from these matrices were 66-103% (6-11) for quizalofop-P-ethyl and 70-114% (8-15) for quizalofop-P. See Table C.1.1 above.
Reliability of the Method [ILV]	An independent laboratory method validation (ILV) was conducted to verify the reliability of method SARS-98-06 for the determination of quizalofop-P-ethyl and quizalofop-P in sunflower seed. The values obtained indicate that method SARS-98-06 is reliable; see Section C.3.
Linearity	The method/detector response was linear (coefficient of determination r^2= 0.99627) within the range of 0.015-0.125 ppm.
Specificity	The control chromatograms provided generally had no peaks above the chromatographic background, and the spiked sample chromatograms contained only the analyte peak of interest. Peaks were well defined and symmetrical. The petitioner noted that if late eluting peaks are observed, run times between injections should be extended to 60 minutes.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for flax seed. Method validation data were included with the flax seed crop field trial study submitted in conjunction with D310869 (refer to the DER for MRID 45089201); adequate recoveries of quizalofop-P-ethyl and quizalofop-P were obtained from flax seed fortified with each analyte at 0.05 and 5.0 ppm. The method validation data are sufficiently representative of the expected residue levels for the flax and sunflower commodities included in the petition associated with D310869.

The petitioner has proposed the current HPLC/UV enforcement method (Dupont Method AMR-153-83, Revision 3, January 1987; MRID 40322410) as a confirmatory method for the HPLC data-collection method.

The petitioner has noted that although there were no indications of possible interference in the validation and analysis of sunflower seed, meal, and oil, late eluting peaks were noticed. In these cases, the run times were extended to 60 minutes between injections.

No radiovalidation data were submitted for the method. Because the extraction procedures of the method are relatively rigorous (reflux in 1 N KOH in methanol for 1.5 hours), no radiovalidation data will be required to support the method.

We note that the method description did not address the issue of determination of the S enantiomers of quizalofop-ethyl and quizalofop. Because the KOH hydrolysis step would convert both the R and S enantiomers of quizalofop-ethyl and quizalofop to MeCHQ, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

C.2. Enforcement Method

The petitioner has not proposed the submitted data-collection method for enforcement purposes.

C.3. Independent Laboratory Validation

An ILV (MRID 44967704) of HPLC Method No. SARS-98-06 was conducted by Ricerca, Inc. (Painesville, OH) using samples of sunflower seed.

Samples of untreated sunflower seed (untreated samples supplied by Texas A & M University) were homogenized in the presence of liquid nitrogen and fortified with quizalofop-P-ethyl and quizalofop-P at 0.05 ppm (LOQ) and 2.0 ppm. Fortified and unfortified samples were analyzed using HPLC Method No. SARS-98-06 as described in Table B.1.1. The petitioner stated that sunflower seed was used for ILV because there are no significant differences in the method extraction/analysis procedures for seed, oil, or meal.

The method was successfully validated on the first trial. The laboratory reported that the method was followed as written with minor modifications in the type of equipment used and volume of standards prepared. Recoveries of quizalofop-P-ethyl and quizalofop-P from sunflower seed samples are reported in Table C.3.1. Total quizalofop-P-ethyl and quizalofop-P residues were below the LOQ (<0.05 ppm) in/on two samples each of unfortified sunflower seed.

The laboratory reported that a set of seven samples could be prepared by one person in 20 hours, with unattended analysis (using an autosampler) requiring 6 hours, and data calculations requiring 2 hours. The total time to complete analysis of a set of seven samples would be 3.5 calendar days. The ILV laboratory recommended some minor changes to the method to improve clarity. It does not appear that the method has been modified to incorporate these recommendations. No critical steps were identified by the ILV laboratory.

TABLE C.3.1. Recovery Results Obtained by an Independent Laboratory Validation of the Data-Collection Method (HPLC Method No. SARS-98-06) for the Determination of Quizalofop-P-Ethyl and Quizalofop-P Residues in Sunflower Seed.

Matrix	Analyte	Spiking Level (ppm)	Recoveries Obtained (%)	Recovery (%)		
				Mean	SD	CV
Sunflower seed	Quizalofop-P-ethyl	0.05	89, 91	92	3.4	3.7
		2.0	92, 97			
	Quizalofop-P	0.05	79, 88	87	6.6	7.6
		2.0	87, 95			

D. CONCLUSION

Adequate method validation data have been submitted for HPLC Method No. SARS-98-06 for the determination of residues of quizalofop-P-ethyl and quizalofop-P in sunflower seed and processed commodities; the data are sufficiently representative of the expected residue levels for flax and sunflower commodities included in the petition associated with D310869. The method was also used for data collection purposes for the analysis of flax seed samples from the flax field trial and processing studies associated with D310869; adequate method validation data were submitted for flax seed with the field trial study.

The petitioner is not proposing the HPLC method (Method No. SARS-98-06) for enforcement purposes. No radiovalidation data have been submitted for the method; however, radiovalidation data are not required because the extraction procedures are rigorous. Adequate independent laboratory validation data have been submitted for the method using samples of sunflower seeds.

E. REFERENCES

None.

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial – Sunflower

Primary Evaluator	S. Oonnithan, Biologist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006 S. Oonnithan
Peer Reviewer	William Drew, Environmental Scientist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006 W T Drew

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850. The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

44967701 Hofen, J. (1999) Magnitude of Quizalofop-P-ethyl and Quizalofop-P Residues in the Raw Agricultural Commodity, Sunflower Seeds: Final Report: Lab Project Number: SARS-98-03: 44963R: 44527. Unpublished study prepared by Stewart Agricultural Research Services, Inc., and ABC Laboratories, Inc. 166 p.

EXECUTIVE SUMMARY:

Nissan Chemical Industries, Ltd. has submitted field trial data for quizalofop-P-ethyl on sunflower seed. Eight trials were conducted in Zone 5(3), Zone 7(4), and Zone 8(1) comprising KS(1), ND(4), SD(2), and TX(1) during the 1998 growing season. An oilseed variety of sunflower was planted at all trial sites, except for the TX trial, which used a non-oilseed variety.

At each test location, two postemergence broadcast applications of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) were made with a 6- to 7-day retreatment interval (RTI) for a total seasonal application rate of ~0.121 lb ai/A. All applications were made using ground equipment in spray volumes of 10-21 gal/A. Samples of mature sunflower seed were harvested 60-61 days after the last application.

Samples of sunflower seed were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl, quizalofop-P and their R & S enantiomers) using high performance liquid chromatography (HPLC) methods (Method No. XAM-38 and Method No. SARS-98-06). The two methods are essentially the same, and were adequate for data collection based on acceptable concurrent method recovery data. The validated limit of quantitation (LOQ) was 0.05 ppm for sunflower seed. Due to the hydrolysis step in the two methods, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage duration of samples from harvest to analysis was 137 days (4.5 months) for sunflower seed. Storage stability data are available for soybean seed, cotton seed, and canola which may be translated to support the storage conditions and intervals of samples from the submitted sunflower field trials.

Residues of total quizalofop-P-ethyl were 0.14-1.32 ppm in/on sunflower seed harvested 60-61 days following two postemergence broadcast applications of the 0.88 lb/gal EC formulation at a total rate of 0.120-0.124 lb ai/A.

No residue decline studies were included in the submission. Because application may be made when the plants are flowering and residues remaining are readily quantifiable in harvested samples, a residue decline study must be conducted.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as conditionally acceptable. The petitioner must submit a residue decline field trial for sunflower: one additional sunflower field trial must be conducted in which samples are collected at 3 to 5 sampling times in addition to the requested preharvest interval (PHI). All sampling times should fall within the crop stage when harvesting could reasonably be expected to occur, and the time points should be approximately equally spaced and, where possible, to represent both shorter and longer PHIs than that requested.

The acceptability of this study for regulatory purposes is addressed in the U.S. EPA Residue Chemistry Summary Document, D310869.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables 1 and 2.

TABLE A.1. Test Compound Nomenclature.

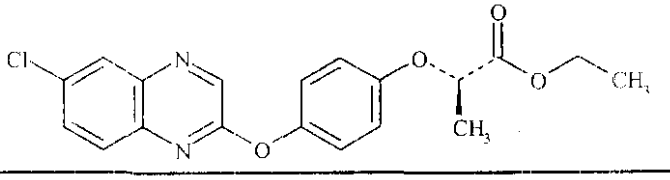
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK$_a$	Not applicable	
Octanol/water partition coefficient	log P$_{OW}$ = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Details of the study site are provided in Table B.1.1. The actual temperature recordings were within the average historical values during the study period for all trials. The actual rainfall average was above the historical rainfall average at three trials (ND-03A, ND-03B, and SD-03A) and below the historical average at two trials (SD-03B and TX-03); however, this did not have a significant impact on crop growth and development at any of the trials. Irrigation was not used at any site.

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year (Trial ID No.)	Soil characteristics [1]			
	Type	%OM [2]	pH	CEC [3]
Hauana, ND; 1998 (SARS-98-ND-03A)	Loam	N/A [4]		
Olivet, SD; 1998 (SARS-98-SD-03A)	Loam	N/A		
Sedan, KS; 1998 (SARS-98-KS-03)	Silt loam	N/A		
Ellendale, ND; 1998 (SARS-98-ND-03B)	Loam	N/A		
Pukwana, SD; 1998 (SARS-98-SD-03B)	Silt loam	N/A		
Velva, ND; 1998 (SARS-98-ND-03C)	Loam	N/A		
New Rockford, ND; 1998 (SARS-98-ND-03D)	Sandy loam	N/A		
Claude, TX; 1998 (SARS-98-TX-03)	Loam	N/A		

[1] Soil characteristic parameters are not applicable since they do not affect the proposed uses.
[2] Organic Matter
[3] Cation exchange capacity
[4] Not applicable

The use pattern followed in the study is summarized in Table B.1.2. At each test location, two postemergence broadcast applications of a 0.88 lb/gal EC formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) were made with a 6- to 7-day RTI. The first application was made at 0.053-0.055 lb ai/A and the second application was made at 0.067-070 lb ai/A, for a total seasonal application rate of 0.120-0.124 lb ai/A. All applications were made using ground equipment in spray volumes of 10-21 gal/A, with an added adjuvant (non-ionic surfactant or petroleum oil) in the spray mixture. The label proposes a PHI of 60 days.

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP [1]	Application					Tank Mix/ Adjuvants [4]
		Method; Timing	Volume [2] (GPA)	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Hauana, ND; 1998 (SARS-98-ND-03A)	0.88 lb/gal EC	Broadcast foliar; flowering	10.1	0.054	---	0.122	Class Preference
		Broadcast foliar; mature	10.1	0.068	7		
Olivet, SD; 1998 (SARS-98-SD-03A)	0.88 lb/gal EC	Broadcast foliar; bud to early flower	20.7	0.053	---	0.120	Activate Plus
		Broadcast foliar; pollinating beginning flower	20.5	0.067	7		
Sedan, KS; 1998 (SARS-98-KS-03)	0.88 lb/gal EC	Broadcast foliar; terminal bud forms miniature floral head	11.5	0.055	---	0.124	Activate Plus
		Broadcast foliar; immature bud elongates above nearest stem leaf	11.8	0.069	7		
Ellendale, ND; 1998 (SARS-98-ND-03B)	0.88 lb/gal EC	Broadcast foliar; flowering	10.2	0.055	---	0.122	Class Preference
		Broadcast foliar; mature	9.9	0.067	7		
Pukwana, SD; 1998 (SARS-98-SD-03B)	0.88 lb/gal EC	Broadcast foliar; beginning pollination	20.7	0.054	---	0.121	Activate Plus
		Broadcast foliar; pollinating, flowering	20.7	0.067	7		
Velva, ND; 1998 (SARS-98-ND-03C)	0.88 lb/gal EC	Broadcast foliar; immature bud elongates above nearest stem leaf	14.9	0.054	---	0.121	X-77
		Broadcast foliar; beginning flowering	14.9	0.067	6		
New Rockford, ND; 1998 (SARS-98-ND-03D)	0.88 lb/gal EC	Broadcast foliar; early bloom/seed development	20.1	0.054	---	0.124	Activate Plus
		Broadcast foliar; seed development	20.3	0.070	7		
Claude, TX; 1998 (SARS-98-TX-03)	0.88 lb/gal EC	Broadcast foliar; midbloom	19.8	0.055	---	0.124	Agri-Dex
		Broadcast foliar; midbloom	19.3	0.069	7		

[1] End-use Product; EPA Reg. No. 352-541
[2] Gallons per acre
[3] Retreatment interval
[4] A non-ionic surfactant was used for all applications at all trials except TX, where a paraffin-base petroleum oil was used, at 0.25% (v/v).

Details of the number of trials and geographical locations are summarized in Table B.1.3.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Sunflower		
	Submitted	Requested [1]	
		Canada	U.S.
1			
1A			
2			
3			
4			
5	3		3
5A			
5B			
6			
7	4		4
7A			
8	1		1
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
Total	8		8

[1] As per OPPTS 860.1500, Tables 1 and 5 for sunflower.

B.2. Sample Collection, Handling, and Preparation

Single untreated and duplicate treated samples of sunflower seed were collected by hand or mechanically from each field trial; mature sunflower seed was harvested 60-61 days after application. The samples were frozen within 4 hours of sampling and shipped frozen to ABC Laboratories, Inc. (Columbia, MO) for residue analysis. Samples (seed including hull) were stored frozen (-34 to 10 °C) at the analytical laboratory until analysis. The petitioner noted a short 10 °C temperature spike during the storage of the samples at the analytical laboratory; all samples remained frozen during the temperature spike. Samples were homogenized in dry ice prior to analysis.

B.3. Analytical Methodology

Samples of sunflower seed were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using HPLC methods, Method No. XAM-38 or Method No. SARS-98-06. The two methods are essentially the same except that the SARS-98-06 method incorporates an increase in the amount of reagents and solvents used in the extraction procedures and in the amount of gel permeation chromatography (GPC) eluate collected. These modifications were made to allow for determination of a larger range of concentrations of the analyte in samples of sunflower seed (>0.5 ppm). Method No. XAM-38 was used for the analysis of samples from all of the trials except for the TX trial, for which Method No. SARS-98-06 was used due to higher residues. A brief description of the methods is included below; for a complete description of the methods, refer to the data evaluation record (DER) for MRID 44967703.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane, and the hexane fraction was cleaned up by GPC. The GPC eluate was concentrated and redissolved in hexane for HPLC analysis with fluorescence detection. Residues of MeCHQ were reported in terms of quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. The validated LOQ was 0.05 ppm for sunflower seed.

We note that based on the hydrolysis step in Methods XAM-38 and SARS-98-06, all reported results for total quizalofop-P-ethyl residues include the residues of R and S enantiomers of quizalofop-P-ethyl and quizalofop-P.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.1. The maximum storage duration of samples from harvest to analysis was 137 days (4.5 months) for sunflower seed. Storage stability data are available for soybean seed, cotton seed, and canola indicating that residues of quizalofop-ethyl and quizalofop are stable for 36 months of frozen storage (PP# 5F3252, 12/18/87, G. Otakie and D220215-17, 2/13/96, F. Griffith)). These data may be translated to support the storage conditions and durations of samples from the sunflower field trials.

TABLE C.1. Summary of Storage Conditions.			
Matrix	Storage Temperature (°C) [1]	Actual Storage Duration [2]	Interval of Demonstrated Storage Stability
Sunflower, seed	-34 to 10	30-137 days (1.0-4.5 months)	Quizalofop-ethyl and quizalofop are stable in/on frozen soybean seed for up to 48 and 36 months, respectively

[1] The petitioner noted a short 10 °C temperature spike during the storage of the samples at the analytical laboratory; all samples remained frozen during the temperature spike.
[2] Actual storage duration from collection to analysis; samples were analyzed within 1-5 days of extraction.

Samples of sunflower seed were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and quizalofop-P) using HPLC methods, Method No. XAM-38, and Method No. SARS-98-06. The methods were adequate for data collection based on acceptable concurrent method recovery data. Recoveries ranged 62-80% (mean = 73%) for sunflower seed fortified with quizalofop-P-ethyl at 0.05 and 0.5 ppm, and analyzed using Method No. XAM-38, and 75-76% for sunflower seed fortified with quizalofop-P-ethyl at 1.0 and 5.0 ppm, and analyzed using Method No. SARS-98-06. The validated LOQ was 0.05 ppm. We note that additional method validation data are available for the methods using sunflower seed fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-5.0 ppm; refer to the DER for MRID 44967703. Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on eight samples of untreated sunflower seed. Concurrent recovery data are summarized in Table C.2.

TABLE C.2. Summary of Concurrent Recoveries of Quizalofop-P-Ethyl from Sunflower Seed.					
Matrix	Method	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean [Std Dev] (%)
Sunflower, seed	XAM-38	0.05	4	62, 68, 74, 74	73 [5.5]
		0.5	4	77, 80, 74, 74	
	SARS-98-06	1.0	1	76	76
		5.0	1	75	

Residue data from each of the sunflower field trials are reported in Table C.3 with a summary of the residue data in Table C.4. Residues of total quizalofop-P-ethyl were 0.14-1.32 ppm in/on sunflower seed harvested 60-61 days following postemergence broadcast applications of the 0.88 lb/gal EC formulation to the ground for a total rate of 0.120-0.124 lb ai/A.

We note that samples from the TX trial were found to contain significantly higher residues (≥2x) than samples from the other trials. The petitioner stated that high residues in these samples were related to physiological changes in the treated sunflowers, which caused the plants to stop growing prematurely. Desiccation occurred sooner in the treated plants than in the control plants, and treated sunflowers had smaller heads and lower yields than the control plants; the petitioner stated that these differences between treated and control plants were not observed in the other trials. Several factors were considered as possible reasons for early desiccation of the plants (i.e., use of a non-oilseed sunflower variety, use of a paraffin-based petroleum oil adjuvant, lower rainfall than normal, spray drift from use of other pesticides in adjoining areas); however, the petitioner stated that no single factor could be identified as the cause. Therefore, it was concluded that the trial represents a worse-case scenario.

TABLE C.3. Residue Data from Sunflower Field Trials with Quizalofop-P-Ethyl.

Trial Identification: City, State; Year (Trial ID No.)	Zone	Crop; Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Total Quizalofop-P-Ethyl Residues (ppm)
Hauana, ND; 1998 (SARS-98-ND-03A)	5	Sunflower; DK 3868	Seed	0.122	60	0.55, 0.64
Olivet, SD; 1998 (SARS-98-SD-03A)	5	Sunflower; Den Beston 754	Seed	0.120	61	0.35, 0.53
Sedan, KS; 1998 (SARS-98-KS-03)	5	Sunflower; NK Sunbred 231	Seed	0.124	60	0.23, 0.25
Ellendale, ND; 1998 (SARS-98-ND-03B)	7	Sunflower; DK 3868	Seed	0.122	60	0.60, 0.61
Pukwana, SD; 1998 (SARS-98-SD-03B)	7	Sunflower; Cargill 187	Seed	0.121	61	0.34, 0.43
Velva, ND; 1998 (SARS-98-ND-03C)	7	Sunflower; Interstate 5077	Seed	0.121	60	0.37, 0.38
New Rockford, ND, 1998 (SARS-98-ND-03D)	7	Sunflower; 821	Seed	0.124	60	0.14, 0.15
Claude, TX, 1998 (SARS-98-TX-03)	8	Sunflower; SUN 891 FI (non-oilseed variety)	Seed	0.124	60	1.30, 1.32

TABLE C.4. Summary of Residue Data from Sunflower Crop Field Trials with Quizalofop-P-Ethyl.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min	Max.	HAFT [1]	Median (STMdR) [2]	Mean (STMR) [3]	Std. Dev.
Sunflower, seed	0.120-0.124	60-61	16	0.14	1.32	1.31	0.41	0.51	0.35

[1] Highest Average Field Trial.
[2] Supervised Trial Median Residue
[3] Supervised Trial Mean Residue

D. CONCLUSION

The submitted sunflower field trial data reflect the use of two postemergence (broadcast ground) applications of a 0.88 lb/gal EC formulation of quizalofop-P-Ethyl at a total rate of 0.120-0.124 lb ai/A, with a PHI of 61 days for sunflower seed. Acceptable methods were used for quantitation of residues in/on sunflower seed.

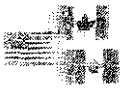
E. REFERENCES

CB Nos.: 2806, 2806, 2810, and 2811
Subject: PP# 5F3252/FAP# 6H5479 Quizalofop Ethyl (Assure®) on Soybeans. Amendment Dates August 31, 1987
From: G. Otakie
To: R. Taylor and Toxicology Branch
Date: 12/18/87
MRIDs: 40322401-40322413, 40336201, and 40337101

DP Barcodes: D220215, D220216, and D220217
Subject: PP# 3F4268/5H5720 - Quizalofop-P-ethyl ester (Assure II) on the Legume Vegetables (Succulent or Dried) and Foliage of Legume Vegetables Crop Groups, Sugar beet Tops, Roots, Molasses, and Cottonseed. Review of the July 27, Sept, 22 and 26, 1995, Amendments. [CBTS #s 16400, 16401, and 16402].
From: F. Griffith
To: R. Taylor and K. Whitby
Dated: 2/13/96
MRID: 43804101

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June/13/2006
EPA Reg. No. 33906-9
Petition No. PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709



Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed - Sunflower

Primary Evaluator S. Oonnithan, Biologist
Registration Action Branch 2
Health Effects Division (7509 P)
Date: June 13, 2006

Peer Reviewer William Drew, Environmental Scientist
Registration Action Branch 2
Health Effects Division (87509 P)
Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

44967702 Hofen, J. (1999) Magnitude of Quizalofop-P-ethyl and Quizalofop-P Residues in Sunflower Seed and Processed Commodities: Final Report: Lab Project Number: SARS-98-04: 44964: 44964R. Unpublished study prepared by Stewart Agricultural Research Services, Inc., and ABC Laboratories, Inc. 999 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted a sunflower seed processing study. In one trial conducted in ND in 1998, sunflower seed was harvested 60 days following a single postemergence broadcast application of the 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) made at 0.121, 0.362, or 0.604 lb ai/A (1x, 2x, and 5x the field trial application rate, respectively). Sunflower seed treated at the highest application rate (5x) was chosen for the processing study. Samples of sunflower seed were harvested 60 days following treatment, and were processed into meal and oil using simulated commercial processing procedures.

Samples of sunflower seed and its processed commodities (meal and oil) were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and quizalofop-P) using high performance liquid chromatography (HPLC) methods (Method No. XAM-38 and Method No. SARS-98-06). The Method No. XAM-38 was used for the analysis of oil samples and Method No. SARS-98-06 was used for the analysis of seed and meal samples. The two methods are essentially the same, and were adequate for data collection based on acceptable concurrent method recovery data. The validated limit of quantitation (LOQ) was 0.05 ppm for all matrices. We note that based on the hydrolysis procedures of Method Nos. XAM-38 and SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage durations of processing study samples from collection to analysis were 172 days (5.7 months) for sunflower seed (RAC), 149 days (4.9 months) for meal, and 34 days (1.1 months) for oil. Storage stability data are available for soybean seed, and cotton seed, meal and oil (PP# 5F3252, 12/18/87, G. Otakie, and D220215-17, 2/13/96, F. Griffith) and may be translated to support the storage conditions and durations of the samples from the sunflower processing study.

Residues of total quizalofop-P-ethyl were 2.45 ppm in/on sunflower seeds treated at the exaggerated rate (5x the field trial application rate). The processing data for meal and oil indicate that residues of total quizalofop-P-ethyl may concentrate slightly in meal (1.2x average processing factor) but do not appear to concentrate in sunflower oil (<0.1x average processing factor).

The reported processing factors do not exceed the theoretical concentration factors for sunflower. According to Tables 2 and 3 of OPPTS 860.1520, the theoretical concentration factors are 4.5x for meal and 2.5x for oil.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the processed commodity residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U.S. EPA Residue Chemistry Summary Document [D310869].

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables 1 and 2.

TABLE A.1. Test Compound Nomenclature.

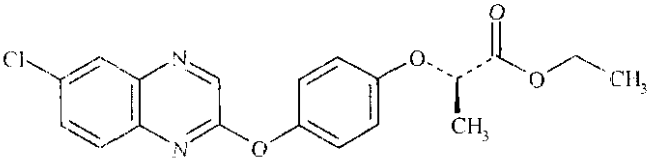
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

The details of the use pattern are summarized in Table B.1.1.

TABLE B.1.1. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume [2] (GPA)	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Velva, ND; 1998 (SARS-98-ND-04)	0.88 lb/gal EC	Broadcast foliar; R5.2, beginning flowering	15.0	0.121	N/A [4]	0.121	X-77 (0.25%)
		Broadcast foliar; R5.2, beginning flowering	15.0	0.362	N/A	0.362	
		Broadcast foliar; R5.2, beginning flowering	15.0	0.604	N/A	0.604	

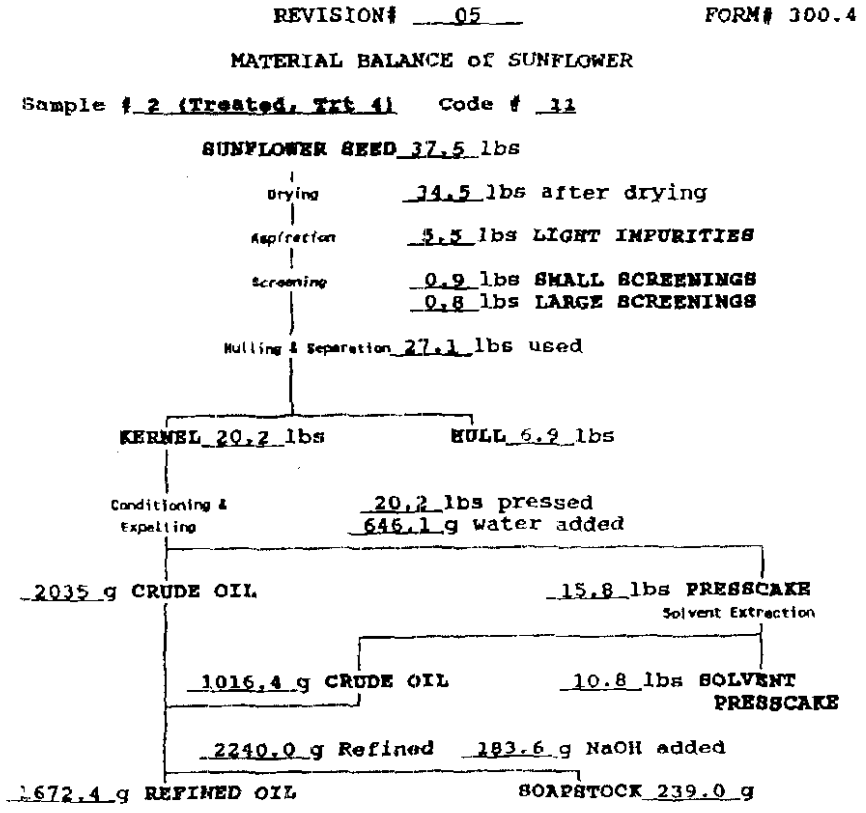
[1] End-use Product: EPA Reg. No. 352-541.
[2] Gallons per acre
[3] Retreatment Interval
[4] Not applicable

B.2. Sample Collection, Handling, and Processing Procedures

Bulk sunflower seed samples from the ND trial were collected using a bundle thresher, and were shipped at ambient temperature within three days of harvest to Texas A & M, Food Protein Research & Development Center (Bryan, TX) for processing. Samples were maintained at the Food Protein Research & Development Center in frozen storage until processing. Sunflower seed samples were processed within 21-25 days of harvest into meal and oil using simulated commercial processing procedures. Sunflower RAC and processed samples were frozen at the processing plant and shipped frozen to ABC Laboratories, Inc. (Columbia, MO) for residue analysis. Samples were stored frozen (-22 to -16 °C) at the analytical laboratory until analysis; samples of sunflower seed (including hull) and meal were homogenized in the presence of dry ice prior to analysis.

The sunflower seed processing procedures are summarized below in Figure 1, which was copied without alteration from MRID 44967702.

FIGURE 1. Processing Flowchart for Sunflower Seed



B.3. Analytical Methodology

Samples of sunflower seed and its processed commodities were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using HPLC methods, Method No. XAM-38 or Method No. SARS-98-06. The two methods are essentially the same except that the SARS-98-06 method incorporates an increase in the amount of reagents and solvents used in the extraction procedures and in the amount of gel permeation chromatography (GPC) eluate collected. These modifications were made to allow for determination of a larger range of concentrations of the analyte in samples (>0.5 ppm). Method No. XAM-38 method was used for the analysis of oil samples and Method No. SARS-98-06 was used for the analysis of seed and meal samples. A brief description of the methods is included below and for a complete description of the methods, refer to the DER for MRID 44967703.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned

up by GPC. The GPC eluate was concentrated and redissolved in hexane for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. The validated LOQ was 0.05 ppm for all sunflower matrices.

We note that based on the hydrolysis procedures of Methods XAM-38 and SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

C. RESULTS AND DISCUSSION

Sunflower seed was harvested 60 days following a single postemergence broadcast application of the 0.88 lb/gal EC formulation at 0.604 lb ai/A (5x the field trial application rate). Sunflower seeds were processed into meal and oil using simulated commercial processing procedures.

Sample storage durations and conditions are summarized in Table C.1. Sunflower seeds and processed commodities were stored frozen following harvest/processing until analysis. The

TABLE C.1. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability
Sunflower, seed	-22 to -16	172 days (5.7 months)	Quizalofop-ethyl and quizalofop are stable in/on frozen soybean seed for up to 48 and 36 months, respectively; and quizalofop is stable in/on cotton seed, meal, and oil stored frozen for up to 28 months.
Sunflower, meal		149 days (4.9 months)	
Sunflower, oil		34 days (1.1 months)	

[1] Storage duration from harvest or processing to analysis. Sunflower seed samples were processed within 21-25 days of harvest; seed and meal samples were analyzed within one day of extraction and oil samples were analyzed within 13 days of extraction.

maximum storage durations of processing study samples from collection to analysis were 5.7 months for sunflower seed, 4.9 months for meal, and 1.1 month for oil. Storage stability data are available for soybean seed indicating that residues of quizalofop-ethyl and quizalofop are stable for up to 36 months of frozen storage (PP# 5F3252, 12/18/87, G. Otakie). In addition, data are available indicating that residues of quizalofop are relatively stable in/on cotton seed, meal, and oil and canola stored frozen for up to 36 months (D220215-17, 2/13/96, F. Griffith). These data may be translated to support the storage conditions and durations of samples from the sunflower processing study.

Concurrent recovery data from the sunflower processing study are presented in Table C.2. Samples of sunflower seed and its processed commodities (meal and oil) were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using HPLC methods. The Method No. XAM-38 was used for the analysis of oil samples and the Method No. SARS-98-06 was used for the

analysis of seed and meal samples. The methods were adequate for data collection based on acceptable concurrent method recovery data.

TABLE C.2. Summary of Concurrent Recoveries of *Quizalofop*-P-Ethyl from Sunflower Matrices.

Matrix	Method	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean (%)
Sunflower, seed	SARS-98-06	1.0	1	72	75
		5.0	1	78	
Sunflower, meal	SARS-98-06	1.0	1	71	75
		5.0	1	79	
Sunflower, oil	XAM-38	0.05	1	76	78
		0.5	1	80	

Recoveries ranged 72-78% for sunflower seed (RAC), and 71-79% for meal fortified with quizalofop-P-ethyl at 1.0-5.0 ppm using Method No. SARS-98-06, and 76-80% for oil fortified at 0.05 and 0.5 ppm using Method XAM-38. We note that additional method validation data are available for the methods using sunflower seed, meal, and oil fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-5.0 ppm; refer to the DER for MRID 44967703. The validated LOQ was 0.05 ppm for sunflower matrices.

Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on one sample each of untreated sunflower seed, meal, and oil.

Residue data from the sunflower processing study are reported in Table C.3. Residues of total quizalofop-P-ethyl were 2.45 ppm in/on sunflower seeds (RAC) treated at the exaggerated rate (5x the field trial application rate). Residues of total quizalofop-P-ethyl were 2.34-3.39 ppm in meal and below the method LOQ in oil processed from the RAC sample bearing quantifiable residues. The processing data indicate that residues of total quizalofop-P-ethyl may concentrate slightly in meal (1.2x average processing factor) but residues do not appear to concentrate in sunflower oil (<0.1x average processing factor).

TABLE C.3. Residue Data from Sunflower Processing Study with Quizalofop-P-Ethyl

RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Total Quizalofop-P-Ethyl Residues (ppm) [1]	Processing Factor
Sunflower	Seed (RAC)	0.604	60	2.45	---
	Meal			2.34, 3.39	1.0x, 1.4x
	Oil			<0.05 (0.034), <0.05 (0.045)	<0.1x, <0.1x

[1] Sunflower seed and meal were analyzed with the SARS-98-06 method and oil was analyzed using the XAM-38 method. The LOQ was 0.05 ppm; actual residue value from the raw data is reported in parentheses.

D. CONCLUSION

The sunflower processing data indicate that residues of quizalofop-P-ethyl may concentrate slightly in meal (1.2x average processing factor). Residues do not appear to concentrate in

sunflower oil (<0.1x average processing factor). Acceptable methods were used for quantitation of residues in/on sunflower seeds and its processed commodities.

E. REFERENCES

CB Nos.: 2806, 2806, 2810, and 2811
Subject: PP# 5F3252/FAP# 6H5479 Quizalofop Ethyl (Assure®) on Soybeans. Amendment Dates August 31, 1987
From: G. Otakie
To: R. Taylor
Date: 12/18/87
MRIDs: 40322401-40322413, 40336201, and 40337101

DP Barcodes: D220215, D220216, and D220217
Subject: PP# 3F4268/5H5720 - Quizalofop-P-ethyl ester (Assure II) on the Legume Vegetables (Succulent or Dried) and Foliage of Legume Vegetables Crop Groups, Sugar beet Tops, Roots, Molasses, and Cottonseed.
From: F. Griffith
To: R. Taylor and K. Whitby
Dated: 2/13/96
MRID: 43804101

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June/13/2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Flax

Primary Evaluator
S. Oonnithan, Biologist. Date: June 13, 2006
Registration Action Branch 2
Health Effects Division (7509 P)

Peer Reviewer
William Drew, Environmental Specialist Date: June 13, 2006
Registration Action Branch 2
Health Effects Division (7509 P)

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45089201 Hofer, J. (2000) Magnitude of Quizalofop-P-Ethyl and Quizalofop-P Residues in the Raw Agricultural Commodity, Flaxseeds: Lab Project Number: SARS-99-10: 10857-1: SARS-99-MN-10. Unpublished study prepared by Stewart Agricultural Research Services, Inc., and Ricerca, Inc. 1396 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted field trial data for quizalofop-P-ethyl on flax seed. Four trials were conducted in Zones 5 (MN and ND; 1 trial each) and 7 (ND; 2 trials) during the 1999 growing season.

At each test location, two postemergence broadcast applications of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) were made with a 6- to 8-day retreatment interval (RTI), for a total seasonal application rate of ~0.161 lb ai/A. All applications were made using ground equipment in spray volumes of 15-20 gal/A. Samples of flax seed were harvested 70-74 days after the last application.

Samples of flax seed were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and its acid metabolite, quizalofop-P) using an high performance liquid chromatography (HPLC) method (Method No. SARS-98-06). This method is adequate for data collection based on acceptable method recoveries conducted prior to and concurrent with the analysis of treated samples. The validated limit of quantitation (LOQ) was 0.05 ppm for flax seed. We note that based on the hydrolysis procedures of Method No. SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage duration of samples from harvest to analysis was 57 days (1.9 months) for flax seed. Storage stability data are available for cottonseed and canola (D220215-17, 2/13/96, F. Griffith) which may be translated to flax seed to support the storage conditions and durations of samples from the submitted flax seed field trials.

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of flax seed harvested 70-74 days after application.

No residue decline study was included in the submission; these data are not required because residues were nonquantifiable in/on mature samples.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document [D310869].

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

TABLE A.1. Test Compound Nomenclature.

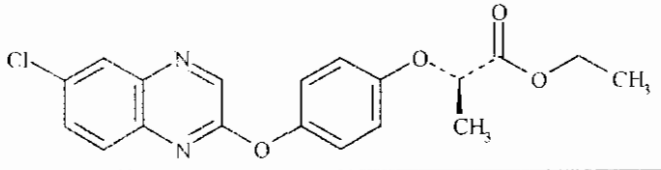
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

The study site details are summarized in Table B.1.1. The actual temperature recordings were within average historical values for the residue study period for all trials. The actual rainfall average in the spring was above the historical rainfall average at all sites which delayed planting; however, this did not have a significant impact on the crop growth and development at any trial. Irrigation was not used at any site.

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year (Trial ID No.)	Soil characteristics [1]			
	Type	%OM [2]	pH	CEC [3]
Dalton, MN; 1999 (SARS-99-MN-10)	Loam	N/A [4]		
Northwood, ND; 1999 (SARS-99-ND-10A)	Loam	N/A		
New Rockford, ND; 1999 (SARS-99-ND-10B)	Sandy loam	N/A		
Velva, ND; 1999 (SARS-99-ND-10C)	Loam	N/A		

[1] These parameters are not applicable since they do not affect the proposed use pattern for this chemical.
[2] Organic matter
[3] Cation exchange capacity
[4] Not applicable

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP[1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI (days)	Total Rate (lb ai/A)	
Dalton, MN; 1999 (SARS-99-MN-10)	0.88 lb/gal EC	1. Broadcast foliar; numerous leaves	20.0	0.080	---	0.161	NIS [3]
		2. Broadcast foliar; numerous leaves	20.0	0.081	7		
Northwood, ND; 1999 (SARS-99-ND-10A)	0.88 lb/gal EC	1. Broadcast foliar; start of branching	20.1	0.081	---	0.162	NIS
		2. Broadcast foliar; branching	20.0	0.081	8		
New Rockford, ND; 1999 (SARS-99-ND-10B)	0.88 lb/gal EC	1. Broadcast foliar; branching	20.1	0.081	---	0.161	NIS
		2. Broadcast foliar; branching	19.6	0.079	7		
Velva, ND; 1999 (SARS-99-ND-10C)	0.88 lb/gal EC	1. Broadcast foliar; vegetative	15.0	0.082	---	0.164	NIS
		2. Broadcast foliar; vegetative	15.0	0.082	7		

[1] End-use Product: EPA Reg. No. 352-541.
[2] Gallons per acre
[3] Non-ionic surfactant; added to all spray mixtures at 0.25% v/v.

Table B.1.2 summarizes the use pattern followed in the study. At each test location, two postemergence broadcast applications of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) were made with a 6-8 day RTI for a total seasonal application rate of 0.161-0.164 lb ai/A. All applications were made using ground equipment in spray volumes of 15-20 gal/A, mixed with a non-ionic surfactant. The label proposes a preharvest interval (PHI) of 70 days. The trial numbers and geographical locations are summarized in Tables B.1.3.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Flax seed		
	Submitted	Requested [1]	
		Canada	U.S.
1			
1A			
2			
3			
4			
5	2		2
5A			
5B			
6			
7	2		3
7A			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
Total	4		5

[1] As per OPPTS 860.1500, Tables 1 and 5 for flax.

We note that a fifth trial was initiated in SD; however, samples from this trial were not analyzed because development of the crop was adversely affected by the spray drift from an adjoining area applied with glyphosate. Information concerning the SD trial is not presented herein.

B.2. Sample Collection, Handling, and Preparation

Single untreated and duplicate treated samples of mature flax seed were collected by hand or mechanically from each field trial; flax seed was harvested 70-74 days after application. All samples were frozen within 3 hours of sampling and shipped frozen to Ricerca, Inc. (Painesville, OH) for residue analysis. Samples were stored frozen (-23 to -20 °C) at the analytical laboratory until analysis; samples were homogenized in the presence of dry ice prior to analysis.

B.3. Analytical Methodology

Samples of flax seed were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using the HPLC method (Method No. SARS-98-06). A brief description of the method is included below; for a complete description of the method, refer to the DER for MRID 44967703.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC). The GPC eluate was concentrated and redissolved in hexane for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. The validated LOQ was 0.05 ppm for flax seed.

In addition to concurrent method validation, the petitioner conducted method validation with flax seed prior to the analysis of the field samples; these data are reported with the concurrent method validation data in Table C.2.

We note that based on the hydrolysis procedures of Method No. SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.1. The maximum storage interval of samples from harvest to analysis was 1.9 months for flax seed. Storage stability data are available for cotton seed and canola indicating that residues of quizalofop-ethyl and quizalofop are stable during up to 36 months, respectively, of frozen storage (D220215-17, 2/13/96, F. Griffith). These data may be translated to support the storage conditions and durations of samples from the flax crop field trials.

Method validation and concurrent recovery data are presented in Table C.2. Samples of flax seed were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using the HPLC method,

(Method No. SARS-98-06). This method is adequate for data collection based on acceptable concurrent method recovery data; recoveries ranged 88-98% for flax seed fortified with quizalofop-P-ethyl at 0.05 and 5.0 ppm. In addition, adequate method recovery data were obtained prior to analysis of the field trial samples; recoveries ranged 86-97% for flax seed fortified with quizalofop-P-ethyl or quizalofop-P at 0.05 and 5.0 ppm. The validated LOQ was 0.05 ppm. Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on four samples of untreated flax seed.

TABLE C.1. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Storage Duration [1]	Interval of Demonstrated Storage Stability
Flax seed	-23 to -20	39-57 days (1.3-1.9 months)	Quizalofop-ethyl and quizalofop are stable in/on frozen soybean seed for up to 48 and 36 months, respectively.

[1] Actual storage duration from collection to analysis; samples were analyzed within 2-4 days of extraction.

TABLE C.2. Summary of Method Validation and Concurrent Recoveries of Quizalofop-P-Ethyl and Quizalofop-P from Flax Seed.

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean [SD] (%)
Method Validation					
Flax seed	Quizalofop-P-ethyl	0.05	3	90, 94, 97	93 [2.5]
		5.0	3	91, 94, 94	
	Quizalofop-P	0.05	3	86, 93, 94	92 [4.6]
		5.0	3	86, 87, 97	
Concurrent Recoveries					
Flax seed	Quizalofop-P-ethyl	0.05	2	92, 98	94 [4.6]
		5.0	2	88, 97	

TABLE C.3. Residue Data from Flax Field Trials with Quizalofop-P-Ethyl.

Trial Identification: City, State; Year (Trial ID No.)	Zone	Crop; Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Total Quizalofop-P-Ethyl Residues (ppm) [1]
Dalton, MN; 1999 (SARS-99-MN-10)	5	Flax; Neche	Seed	0.161	74	<0.05, <0.05
Northwood, ND; 1999 (SARS-99-ND-10A)	5	Flax; Omega	Seed	0.162	71	<0.05, <0.05
New Rockford, ND; 1999 (SARS-99-ND-10B)	7	Flax; Omega	Seed	0.161	70	<0.05, <0.05
Velva, ND; 1999 (SARS-99-ND-10C)	7	Flax; Neche	Seed	0.164	70	<0.05, <0.05

[1] The validated method LOQ was 0.05 ppm for flax seed.

Residue data from the flax field trials are reported in Table C.3 and a summary is presented in Table C.4. The residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm)

in/on flax seed harvested 70-74 days following postemergence broadcast applications of the 0.88 lb/gal EC formulation, at a total rate of 0.161-0.164 ppm.

TABLE C.4. Summary of Residue Data from Flax Field Trials with Quizalofop-P-Ethyl.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels [1] (ppm)						
			n	Min.	Max.	HAFT [2]	Median (STMdR) [3]	Mean (STMR) [4]	Std. Dev.
Flax, seed	0.161-0.164	70-74	8	<0.05	<0.05	<0.05	<0.025	<0.025	0

[1] The LOQ was 0.05 ppm. In calculating the median, mean, and standard deviation, half the LOQ was used for residues reported below the LOQ in Table C.3.
[2] Highest Average Field Trial.
[3] Supervised Trial Median Residue
[4] Supervised Trial Mean Residue

D. CONCLUSION

The submitted flax field trial data reflect the use of two postemergence (broadcast ground) applications of a 0.88 lb/gal EC formulation of quizalofop-P-ethyl at a total rate of 0.161-0.164 lb ai/A, with a PHI of 70-74 days for flax seed. An acceptable method was used for quantitation of residues in/on flax seed.

E. REFERENCES

DP Barcode: D220215-217
Subject: PP# 3F4268/5H5720 - Quizalofop-P-ethyl ester (Assure II) on the Legume Vegetables (Succulent or Dried) and Foliage of Legume Vegetable Crop Groups, Sugar beet Tops, Roots, Molasses, and Cottonseed.
From: F. Griffith
To: R. Taylor and K. Whitby
Dated: 2/13/96
MRID: 43804101

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-Ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed - Flax

Primary Evaluator	S. Oonnithan, Biologist. Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006
Peer Reviewer	William Drew, Environmental Scientist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45089202 Hofen, J. (2000) Magnitude of Quizalofop-P-Ethyl and Quizalofop-P Residues in Flaxseed and Processed Commodity, Meal: Lab Project Number: SARS-99-11: 010857-2: 99-1820. Unpublished study prepared by Stewart Agricultural Research Services, Inc., and Ricerca, Inc. 391 p

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted a processing study with flax seed. In one trial conducted in MN, flax seed was harvested 74 days following a single postemergence broadcast application of the 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) at 0.323 lb ai/A (2x the field trial application rate) or 0.81 lb ai/A (5x the field trial application rate). Flax seed treated at the highest application rate was chosen for the processing study.

Samples of flax seed were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and its acid metabolite, quizalofop-P) using a high performance liquid chromatography (HPLC) method (Method No. SARS-98-06). This method is adequate for data collection based on acceptable concurrent method recoveries. The validated limit of quantitation (LOQ) was 0.05 ppm for flax seed. We note that based on the hydrolysis procedures of Method No. SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage duration of the study samples from collection to analysis was 1.2 months for flax seed. Storage stability data are available for soybean seed (PP# 5F3252, 12/18/87, G. Otakie) which may be translated to support the storage conditions and durations of samples from the submitted study.

Residues of total quizalofop-P-ethyl were less than the LOQ (<0.05 ppm) in/on flax seed treated at the exaggerated rate (5x the field trial application rate), therefore, raw agricultural commodity (RAC) samples were not processed into meal.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the processed commodity residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document [D310869].

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

TABLE A.1. Test Compound Nomenclature.

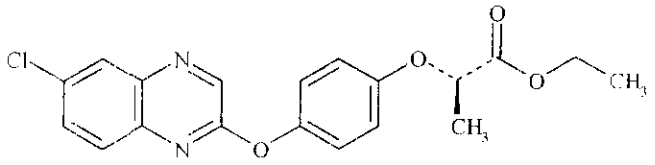
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

Details of the use pattern followed in the study are provided in Table B.1.1. Two plots were treated with a single postemergence broadcast application of the 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541), the plot #1 at 0.323 lb ai/A (2x the field trial application rate) and the plot #2 at 0.81 lb ai/A (5x the field trial application rate). The label proposes a preharvest interval (PHI) of 70 days. Only the flax crop treated at the 5x application rate was chosen for the processing study.

TABLE B.1.1. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Dalton, MN; 1999 (SARS-99-MN-11)	0.88 lb/gal EC	Broadcast foliar; numerous leaves	12.04	0.323	N/A	0.323 (2x)	X-77 (0.25%)
			120.6	0.81	NA	0.81 (5x)	

[1] End-use Product; EPA Reg. No. 352-541.
[2] Gallons per acre
[3] Retreatment Interval; not applicable (N/A) because a single application was made.

B.2. Sample Collection, Handling, and Processing Procedures

Bulk flaxseed samples from the MN trial site were collected using a combine and shipped at ambient temperatures within one day of harvest to Texas A. & M., Food Protein Research & Development Center (Bryan, TX) for processing. Samples were stored frozen at the Food Protein Research & Development Center. A subsample of the RAC sample was taken and shipped frozen to Ricerca, Inc. for initial residue analysis. Flax seed samples were stored frozen at the analytical laboratory until analysis; samples (seed including hull) were homogenized in the presence of dry ice prior to analysis. Because nonquantifiable residues of total quizalofop-P-ethyl were found in the RAC, the flax seed sample was not processed into meal.

B.3. Analytical Methodology

Samples of flax seed were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using an HPLC method (Method No. SARS-98-06). A brief description of the method is included below; for a complete description of the method, refer to the DER for MRID 44967703.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC). The GPC eluate was concentrated and redissolved in hexane for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-

P-ethyl equivalents using a molecular weight conversion factor of 1.917. The validated LOQ was 0.05 ppm for flax seed.

We note that based on the hydrolysis procedures of Method No. SARS-98-06, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

C. RESULTS AND DISCUSSION

Flax seed was harvested 74 days following a single postemergence broadcast application of the 0.88 lb/gal EC formulation at 0.81 lb ai/A (5x the field trial application rate).

Sample storage durations and conditions are summarized in Table C.1. Flax seed samples were stored frozen prior to analysis. The maximum storage duration of the study samples from harvest to analysis was 36 days (1.2 months). Storage stability data are available for soybean seed indicating that residues of quizalofop-ethyl and quizalofop are stable during up to 48 and 36 months, respectively, of frozen storage (PP# 5F3252, 12/18/87, G. Otakie). These data may be translated to support the storage conditions and durations of samples from the submitted flax study.

TABLE C.1. Summary of Storage Conditions.

Matrix (RAC or Extract)	Storage Temperature °C)	Actual Storage Duration [1]	Duration of Demonstrated Storage Stability
Flax seed (RAC)	Frozen	36 days (1.2 months)	Quizalofop-ethyl and quizalofop are stable in/on frozen soybean seed for up to 48 and 36 months, respectively.

[1] Storage duration from collection to analysis. All samples were analyzed within 4 days of extraction.

Concurrent recovery data from the flax seed processing study are presented in Table C.2. Samples of flax seed were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using an HPLC method, Method No. SARS-98-06. This method is adequate for data collection based on acceptable concurrent method recovery data. Recoveries ranged 85-92% for flax seed fortified with quizalofop-P-ethyl at 0.05 and 5.0 ppm. We note that additional method validation data for flax seed fortified with quizalofop-P-ethyl or quizalofop-P were submitted in conjunction with the flax field trials (refer to the DER for MRID 45089201). The validated LOQ was 0.05 ppm. Apparent residues of total quizalofop-P-ethyl were below the method LOQ in/on one sample of untreated flax seed.

TABLE C.2. Summary of Concurrent Recoveries of Total Quizalofop-P-Ethyl from Flax Seed

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean (%)
Flax seed	0.05	1	85	89
	5.0	1	92	

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on flax seed treated at the exaggerated rate (5x the field trial application rate), therefore, RAC samples were not processed into meal.

TABLE C.3. Residue Data from Flax Seed Processing Study with Quizalofop-P-Ethyl.

RAC	RAC or Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Total Quizalofop-P-Ethyl Residues (ppm) [1]	Processing Factor
Flax	Seed (RAC)	0.81	74	<0.05 (0.047)	--

[1] The LOQ was 0.05 ppm for flax seed; the actual residue value is reported in parentheses.

D. CONCLUSION

Total quizalofop-P-ethyl residues in/on flax seed were nonquantifiable following one postemergence treatment at an exaggerated rate representing 5x the field trial application rate; because residues were below the LOQ in RAC, it was not processed. An acceptable method was used for quantitation of residues in/on flax seed.

E. REFERENCES

CB Nos.: 2806, 2806, 2810, and 2811
Subject: PP# 5F3252/FAP # 6H5479 Quizalofop Ethyl (Assure®) on Soybeans. Amendment Dates August 31, 1987
From: G. Otakie
To: R. Taylor and Toxicology Branch
Date: 12/28/87
MRIDs: 40322401-40322413, 40336201, and 40337101

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Wheat

Primary Evaluator: S. Oonnithan, Biologist
Registration Action Branch 2
Health Effects Division (7509 P)
Date: June 13, 2006

Peer Reviewer: William Drew, Environmental Scientist
Registration Action Branch 2
Health Effects Division (7509 P)
Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850. The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45885801 Carringer, S. (2002) Magnitude of the Residue of Quizalofop-P-Ethyl and Quizalofop-P in Wheat Raw Agricultural and Processed Commodities: Final Study Report: Lab Project Number: TCI-01-006-01; TCI-01-006-02; TCI-01-006-03. Unpublished study prepared by Morse Laboratories, Inc. 593 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted field trial data for quizalofop-P-ethyl on wheat. Thirty-two trials were conducted in the U.S.(15) and Canada(17) during the 2001 and 2002 growing season. The U.S. trials were conducted in Zones 2 (NC 1 trial), 4 (AR; 1 trial), 5 (KS, NE, and ND; 3 trials), 6 (OK and TX; 3 trials), 7 (ND, NE, and SD; 3 trials), 8 (KS and TX; 3 trials), and 11 (ID; 1 trial). The Canadian trials were conducted in Zones 5 (ON; 2 trials), 7 (AB and SK; 2 trials), 7A (AB; 3 trials), and 14 (AB, MB, and SK; 10 trials). Nine trials were conducted on winter wheat and the remainder were conducted on spring wheat.

At each test location, a single preplant broadcast application of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) was made to the soil surface at ~0.068 lb ai/A, on or the day before planting. All applications were made using ground equipment in volumes of 4.9-20.7 gal/A. Samples of wheat forage were harvested 21-209 days after application; samples of wheat hay were harvested 55-231 days after application and dried in the field for 1-10 days; and samples of mature wheat grain and straw were harvested 90-272 days after application.

Samples of wheat matrices were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and its acid metabolite, quizalofop-P) using a high performance liquid chromatography (HPLC) method (Morse Method Meth-147). This method is adequate for data collection based on acceptable method recoveries. The validated limit of quantitation (LOQ) was 0.05 ppm and

the defined limit of detection (LOD) was 0.017 ppm for all wheat matrices. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage durations of samples from harvest to analysis were 7.2 months for wheat forage, 6.8 months for wheat hay, 4.2 months for wheat grain, and 5.6 months for wheat straw. Adequate storage stability data were submitted for wheat matrices (refer to the 860.1380 DER for MRID 45885801) to support the storage conditions and durations of wheat samples from the submitted field trials.

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of wheat forage harvested 21-209 days after application, wheat hay harvested 55-231 days after application, and wheat grain and straw harvested 90-272 days after application.

No residue decline study or aspirated grain fractions data were included in the submission. These data are not required because application was made prior to crop emergence.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D310869.

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

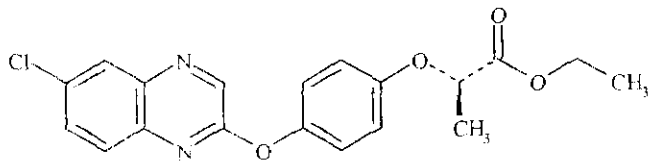
TABLE A.1. Test Compound Nomenclature.	
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound *Quizalofop-P-Ethyl*.			
Parameter	Value		Reference
Melting point	76.0-77.0 °C (pure form)		CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)		
Density	1.35 g/cm^3 at 20 °C (pure form)		
Water solubility	0.4 ppm (20 °C)		
Solvent solubility		g/L at 20 °C	
	acetone	650	
	benzene	680	
	carbon disulfide	660	
	chloroform	1350	
	cyclohexanone	440	
	dichloromethane	1970	
	dimethyl sulfoxide	200	
	ethanol	22	
	n-hexane	5	
	methanol	22	
	tetrahydrofuran	1160	
	toluene	430	
	xylene	360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)		
Dissociation constant, pK_a	Not applicable		
Octanol/water partition coefficient	log P_{OW} = 4.66		
UV/visible absorption spectrum	Not available		

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

The study site details are summarized in Table B.1.1.

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year (Trial ID No.)	Soil characteristics [1]			
	Type	%OM [2]	pH	CEC [3]
Rose Hill, NC; 2001 (TCI-01-006-01)	Loamy sand	N/A [4]		
Proctor, AR; 2001 (TCI-01-006-02)	Silt loam	N/A		
York, NE; 2001 (TCI-01-006-03)	Silt loam	N/A		
New Rockford, ND; 2001 (TCI-01-006-04)	Loam	N/A		
Andale, KS; 2001 (TCI-01-006-05)	Silt loam	N/A		
Sheffield, ON; 2001 (TCI-01-006-06)	Silt loam	N/A		
Branchton, ON; 2001 (TCI-01-006-07)	Loam	N/A		
Brookshire, TX; 2001 (TCI-01-006-08)	Sandy loam	N/A		
Grand Island, NE; 2001 (TCI-01-006-09)	Silt loam	N/A		
Lake Andes, SD; 2001 (TCI-01-006-10)	Silty clay loam	N/A		
Velva, ND; 2001 (TCI-01-006-11)	Loam	N/A		
Conquest, SK; 2001 (TCI-01-006-12)	Sandy loam	N/A		
Delisle, SK; 2001 (TCI-01-006-13)	Loam	N/A		
Taber, AB; 2001 (TCI-01-006-14)	Loam	N/A		
Warner, AB; 2001 (TCI-01-006-15)	Clay loam	N/A		
Barnwell, AB; 2001 (TCI-01-006-16)	Sandy loam	N/A		
Greensburg, KS; 2001 (TCI-01-006-18)	Silt loam	N/A		
Eakly, OK; 2001 (TCI-01-006-19)	Sandy loam	N/A		
Uvalde, TX; 2001 (TCI-01-006-20)	Clay loam	N/A		
Levelland, TX; 2001 (TCI-01-006-21)	Sandy loam	N/A		
Littlefield, TX; 2001 (TCI-01-006-22)	Loam	N/A		
Payette, ID; 2001 (TCI-01-006-23)	Loam	N/A		
Brookdale, MB; 2001 (TCI-01-006-24)	Loam/clay loam	N/A		
Clanwilliam, MB; 2001 (TCI-01-006-25)	Clay loam	N/A		
Edmonton; AB; 2001 (TCI-01-006-26)	Clay loam	N/A		
Wetaskiwin, AB; 2001 (TCI-01-006-27)	Loam	N/A		
Wakaw, SK; 2001 (TCI-01-006-28)	Silty loam/loam	N/A		
Minto, MB; 2001 (TCI-01-006-29)	Loam/clay loam	N/A		
Lancombe, AB; 2001 (TCI-01-006-30)	Silt loam	N/A		
Lancombe, AB; 2001 (TCI-01-006-31)	Silt loam	N/A		
Rosthern, SK; 2001 (TCI-01-006-32)	Clay/ loam	N/A		
Hepburn, SK; 2001 (TCI-01-006-33)	Clay/ loam	N/A		

[1] These parameters are not applicable since they do not affect the proposed use pattern for this chemical.
[2] Organic matter
[3] Cation exchange capacity
[4] Not applicable

The actual temperature recordings were within average historical values for the residue study period with the exception of 2 trials (-02 and -20) in which a spring freeze caused some crop injury; the petitioner noted that sufficient crops were available at these two trials to provide adequate sample for the study. The actual rainfall average was below the historical rainfall

average at many sites; however, this did not have a significant impact on any site, with the exception of one trial conducted in KS (TCI-01-006-17) in which the crop was lost due to drought conditions. Information and further results for this trial are not presented herein. Irrigation was used to supplement rainfall in 10 trials.

The use pattern followed for the study is summarized in Table B.1.2. At each test location, a single preplant broadcast application of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) was made to the soil surface at 0.065-0.073 lb ai/A, on or the day before planting. All applications were made using ground equipment in spray volumes of 4.9-20.7 gal/A, containing a petroleum-based crop oil concentrate adjuvant. The label did not propose a preharvest interval (PHI) for the raw agricultural commodity (RAC), wheat grain.

TABLE B.1.2. Study Use Pattern.

Location: City, State; Year, (Trial ID)	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI [3] (days)	*Total Rate* (lb ai/A)	
Rose Hill, NC; 2001 (TCI-01-006-01)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.2	0.069	NA [4]	0.069	Crop Oil [5]
Proctor, AR; 2001 (TCI-01-006-02)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	16.2	0.068	NA	0.068	Crop Oil
York, NE; 2001 (TCI-01-006-03)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	19.9	0.068	NA	0.068	Crop Oil
New Rockford, ND; 2001 (TCI-01-006-04)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.0	0.069	NA	0.069	Crop Oil
Andale, KS; 2001 (TCI-01-006-05)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.2	0.068	NA	0.068	Crop Oil
Sheffield, ON; 2001 (TCI-01-006-06)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.6	0.069	NA	0.069	Crop Oil
Branchton, ON; 2001 (TCI-01-006-07)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.8	0.067	NA	0.067	Crop Oil
Brookshire, TX; 2001 (TCI-01-006-08)	0.88 lb/gal EC	Preplant broadcast; on the day of planting	5.07	0.069	NA	0.069	Crop Oil
Grand Island, NE; 2001 (TCI-01-006-09)	0.88 lb/gal EC	Preplant broadcast; on the day of planting	5.0	0.067	NA	0.067	Crop Oil
Lake Andes, SD; 2001 (TCI-01-006-10)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	17.0	0.067	NA	0.067	Crop Oil
Velva, ND; 2001 (TCI-01-006-11)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.2	0.069	NA	0.069	Crop Oil
Conquest, SK; 2001 (TCI-01-006-12)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	4.9	0.067	NA	0.067	Crop Oil
Delisle, SK; 2001 (TCI-01-006-13)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	12.1	0.068	NA	0.068	Crop Oil
Taber, AB; 2001 (TCI-01-006-14)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.9	0.069	NA	0.069	Crop Oil
Warner, AB; 2001 (TCI-01-006-15)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.8	0.069	NA	0.069	Crop Oil
Barnwell, AB; 2001 (TCI-01-006-16)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.7	0.068	NA	0.068	Crop Oil
Greensburg, KS; 2001 (TCI-01-006-18)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.9	0.066	NA	0.066	Crop Oil

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Wheat

TABLE B.1.2. Study Use Pattern.

Location: City, State; Year, (Trial ID)	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Eakly, OK; 2001 (TCI-01-006-19)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	12.8	0.067	NA	0.067	Crop Oil
Uvalde, TX; 2001 (TCI-01-006-20)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	17.6	0.067	NA	0.067	Crop Oil
Levelland, TX; 2001 (TCI-01-006-21)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	20.1	0.069	NA	0.069	Crop Oil
Littlefield, TX; 2001 (TCI-01-006-22)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	20.2	0.069	NA	0.069	Crop Oil
Payette, ID; 2001 (TCI-01-006-23)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	20.7	0.071	NA	0.071	Crop Oil
Brookdale, MB; 2001 (TCI-01-006-24)	0.88 lb/gal EC	Preplant broadcast; on the day of planting	11.9	0.066	NA	0.066	Crop Oil
Clanwilliam, MB; 2001 (TCI-01-006-25)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.9	0.066	NA	0.066	Crop Oil
Edmonton, AB; 2001 (TCI-01-006-26)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.8	0.069	NA	0.069	Crop Oil
Wetaskiwin, AB; 2001 (TCI-01-006-27)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.2	0.065	NA	0.065	Crop Oil
Wakaw, SK; 2001 (TCI-01-006-28)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.3	0.073	NA	0.073	Crop Oil
Minto, MB; 2001 (TCI-01-006-29)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.1	0.069	NA	0.069	Crop Oil
Lancombe, AB; 2001 (TCI-01-006-30)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.8	0.070	NA	0.070	Crop Oil
Lancombe, AB; 2001 (TCI-01-006-31)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.6	0.068	NA	0.068	Crop Oil
Rosthern, SK; 2001 (TCI-01-006-32)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.6	0.069	NA	0.069	Crop Oil
Hepburn, SK; 2001 (TCI-01-006-33)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.8	0.070	NA	0.070	Crop Oil

[1] End-use Product: EPA Reg. No. 352-541
[2] Gallons per acre
[3] Retreatment Interval
[4] NA - Not applicable
[5] Petroleum based crop oil; added to all spray mixtures at 1% v/v.

Details of the number of trials and geographical locations are summarized in Table B.1.3.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Wheat		
	Submitted	Requested [1]	
		Canada	U.S.
1			
1A			
2	1		1 (1)
3			
4	1		1 (1)
5	5	2	5 (3)
5A			

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Wheat		
	Submitted	Requested [1]	
		Canada	U.S.
5B			
6	3 (2 near the border between Zones 6 and 8)		1 (1)
7	5	7	5 (4)
7A	3 (2 near the border between Zones 7 and 7A)	1	
8	3		6 (4)
9			
10			
11	1		1 (1)
12			
13			
14	10	10	
15			
16			
17			
18			
19			
20			
21			
Total	32	20	20 (15)

[1] As per OPPTS 860.1500, Tables 1 and 5 and Directive 98-02; Section 9 for wheat as an individual crop; the values in parentheses represent a 25% reduction in the number of trials required, due to pesticide use resulting in no quantifiable residues.

B.2. Sample Collection, Handling, and Preparation

Single untreated and duplicate treated samples of the wheat matrices were collected by hand or using a thresher/combine from each field trial. The PHI of wheat matrices were: (i) wheat forage at the 6-8 inch stem elongation (jointing) growth stage at 21-54 days for spring wheat and 66-209 days for winter wheat; (ii) wheat hay at the early flowering (boot) to soft dough stage at 55-84 days for spring wheat, and 141-231 days for winter wheat); (iii) mature wheat grain and straw at 90-132 days for spring wheat and 177-272 days for winter wheat. Wheat forage and hay samples were dried in the field for 1-10 days before collection. All samples were frozen within 5 hours of sampling and shipped frozen to the Morse Laboratories, Inc. (Sacramento, CA) for residue analysis. Samples were stored frozen (-20 ± 5 °C) at the analytical laboratory until analysis; samples were homogenized in the presence of dry ice prior to analysis.

B.3. Analytical Methodology

Samples of wheat forage, hay, grain, and straw were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using an HPLC method (Morse Method Meth-147). A description of the method is included below; for a complete description of the method, refer to the D310869 DER for Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities, MRIDs 45885803 and 45858504.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC); the hexane fractions of wheat hay and straw were cleaned up by silica solid-phase extraction prior to GPC cleanup. The GPC eluate was concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop. The validated LOQ was 0.05 ppm for wheat forage, hay, grain and straw, and the defined LOD was 0.017 ppm for all matrices.

We note that the petitioner calculated LOQ and LOD values for each wheat matrix using the standard deviation of method recoveries at the LOQ. But, for reporting the results, the petitioner used the validated LOQ value of 0.05 ppm (higher than calculated LOQs) and the defined LOD value of 0.017 ppm (higher than calculated LODs).

Concurrent method validation data were collected for the wheat matrices (see Table C.2), including at the defined LOD level. Recoveries at the LOD fortification level were 58-125% in wheat forage, hay, grain and straw. These data were collected to verify the LOD and are not included with the concurrent method recovery data in Table C.2.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.1. The maximum storage intervals of samples from harvest to analysis were 220 days (7.2 months) for wheat forage, 207 days (6.8 months) for wheat hay, 128 days (4.2 months) for wheat grain, and 169 days (5.6 months) for wheat straw. To support sample storage conditions and intervals, the petitioner included storage stability data on wheat matrices (D310869; Storage Stability – Wheat; DER for MRID 45885801). These data demonstrate that residues of quizalofop-P-ethyl and quizalofop-P are stable in/on wheat forage, hay, grain, and straw stored frozen for ~11-13 months.

TABLE C.1. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability [2]
Wheat, forage	-20 ± 5	65-220 days (2.1-7.2 months)	Quizalofop-P-ethyl and quizalofop-P are stable in/on fortified wheat forage and grain stored frozen for 12.7 months, and wheat hay and straw stored frozen for 11.2 months.
Wheat, hay		59-207 days (1.9-6.8 months)	
Wheat, grain		32-128 days (1.1-4.2 months)	
Wheat, straw		68-169 days (2.2-5.6 months)	

[1] Actual storage duration from collection to analysis; samples were analyzed within 4-16 days of extraction.
[2] D310869 Storage Stability DER for MRID 45885801

Concurrent method recovery data are presented in Table C.2. Wheat matrices were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using an HPLC method (Morse Method Meth-147). The method is adequate for data collection based on acceptable concurrent method recovery data; overall recoveries ranged 70-95% for forage, 71-98% for hay, 72-98% for grain, and 64-95% for straw fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-0.20 ppm. The validated LOQ was 0.05 ppm for wheat commodities. Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on all samples of untreated forage, hay, grain, and straw.

TABLE C.2. Summary of Concurrent Recoveries of Quizalofop-P-Ethyl and Quizalofop-P from Wheat Matrices.

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean [Std. Dev.] %
Wheat, forage	Quizalofop-P-ethyl	0.05	9	70, 72, 81, 83, 84, 87, 90, 92, 95	84 [8.3]
		0.1	2	77, 82	
		0.2	1	95	
	Quizalofop-P	0.05	7	70, 71,71, 75, 78, 82, 83	76 [6.0]
		0.1	2	72, 73	
		0.2	1	87	
Wheat, hay	Quizalofop-P-ethyl	0.05	7	73, 73, 76, 86, 86, 91, 98	83 [8.0]
		0.1	2	79, 85	
		0.2	1	84	
	Quizalofop-P	0.05	7	71, 79, 82, 83, 85, 88, 92	81 [6.0]
		0.1	2	77, 78	
		0.2	1	78	
Wheat, grain	Quizalofop-P-ethyl	0.05	9	72, 75, 87, 88, 90, 91, 95, 96, 98	88 [7.3]
		0.1	4	84, 88, 91, 91	
		0.2	1	88	
	Quizalofop-P	0.05	8	74, 78, 80, 80, 82, 82, 92, 94	82 [5.8]
		0.1	2	80, 81	
		0.2	1	83	
Wheat, straw	Quizalofop-P-ethyl	0.05	9	70, 76, 76, 78, 79, 86, 91, 95, 95	83 [8.0]
		0.1	2	78, 81	
		0.2	1	86	
	Quizalofop-P	0.05	6	64, 70, 75, 77, 80, 83	73 [6.2]
		0.1	2	69, 69	
		0.2	1	69	

Residue data from the wheat field trials are reported in Table C.3. A summary of residue data for wheat forage, hay, grain, and straw is presented in Table C.4. Following a single preplant application of the 0.88 lb/gal EC formulation at 0.065-0.073 lb ai/A, residues of total quizalofop-P-ethyl were less than the LOQ in/on all samples of wheat forage harvested 21-209 days after application, wheat hay harvested 55-231 days after application, and wheat grain and straw harvested 90-272 days after application.

Treatment-related phytotoxicity was observed with the wheat plants from 6 trials, causing stunting and stand reduction shortly after crop emergence; however, the symptoms decreased with time and were not present at crop maturity. The petitioner reported that the phytotoxicity appeared to have no negative impact on the study results.

TABLE C.3. Residue Data from Wheat *Field Trials with Quizalofop-P-Ethyl.*

Location; City, State; Year (Trial ID)	Zone	Crop; Variety	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm) [2]
Rose Hill, NC; 2001 (TCI-01-006-01)	2	Winter Wheat; Coker 9803	0.069	Forage	162	ND, ND [3]
				Hay	192 (4)	ND, ND
				Grain	222	ND, ND
				Straw	222	ND, ND
Proctor, AR; 2001 (TCI-01-006-02)	4	Winter Wheat; Pioneer 2684	0.068	Forage	186	ND, ND
				Hay	214 (5)	ND, ND
				Grain	244	ND, ND
				Straw	244	ND, ND
York, NE; 2001 (TCI-01-006-03)	5	Spring Wheat; Forge HRS	0.068	Forage	50	ND, ND
				Hay	66 (4)	ND, ND
				Grain	104	ND, ND
				Straw	104	ND, ND
New Rockford, ND; 2001 (TCI-01-006-04)	5	Spring Wheat; 2375	0.069	Forage	33	ND, ND
				Hay	58 (4)	ND, ND
				Grain	92	ND, ND
				Straw	92	ND, ND
Andale, KS; 2001 (TCI-01-006-05)	5	Winter Wheat; 2137	0.068	Forage	197	ND, ND
				Hay	219 (10)	ND, ND
				Grain	255	ND, ND
				Straw	255	ND, ND
Sheffield, ON; 2001 (TCI-01-006-06)	5	Spring Wheat; Celtic	0.069	Forage	40	ND, ND
				Hay	67 (2)	ND, ND
				Grain	97	ND, ND
				Straw	97	ND, ND
Branchton, ON; 2001 (TCI-01-006-07)	5	Spring Wheat; Quantum	0.067	Forage	40	ND, ND
				Hay	67 (2)	ND, ND
				Grain	96	ND, ND
				Straw	96	ND, ND
Brookshire, TX; 2001 (TCI-01-006-08)	6	Winter Wheat; Ogallala	0.069	Forage	115	ND, ND
				Hay	216 (3)	ND, ND
				Grain	237	ND, ND

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DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Wheat

TABLE C.3. Residue Data from Wheat Field Trials with Quizalofop-P-Ethyl.

Location: City, State; Year (Trial ID)	Zone	Crop; Variety	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm) [2]
				Straw	237	ND, ND
Grand Island, NE; 2001 (TCI-01-006-09)	7	Spring Wheat; Forge HRS	0.067	Forage	41	ND, ND
				Hay	63 (2)	ND, ND
				Grain	96	ND, ND
				Straw	96	ND, ND
Lake Andes, SD; 2001 (TCI-01-006-10)	7	Spring Wheat; Forge HRS	0.067	Forage	37	ND, ND
				Hay	59 (2)	ND, ND
				Grain	95	ND, (0.017)
				Straw	95	ND, ND
Velva, ND; 2001 (TCI-01-006-11)	7	Spring Wheat; Alsen	0.069	Forage	37	ND, ND
				Hay	65 (1)	ND, ND
				Grain	96	ND, ND
				Straw	96	ND, ND
Conquest, SK; 2001 (TCI-01-006-12)	7	Spring Wheat; AC Cadillac	0.067	Forage	33	ND, ND
				Hay	63 (7)	ND, ND
				Grain	102	ND, ND
				Straw	102	ND, ND
Delisle, SK; 2001 (TCI-01-006-13)	7	Spring Wheat; AC Cadillac	0.068	Forage	34	ND, ND
				Hay	64 (7)	ND, ND
				Grain	103	ND, ND
				Straw	103	ND, (0.017)
Taber, AB; 2001 (TCI-01-006-14)	7A	Spring Wheat; AC Intrepid	0.069	Forage	41	ND, ND
				Hay	64 (3)	ND, ND
				Grain	104	ND, ND
				Straw	104	ND, ND
Warner, AB; 2001 (TCI-01-006-15)	7A	Spring Wheat; AC Intrepid	0.069	Forage	40	ND, ND
				Hay	63 (3)	ND, ND
				Grain	99	ND, ND
				Straw	99	ND, ND
Barnwell, AB; 2001 (TCI-01-006-16)	7A	Spring Wheat; AC Barrie	0.068	Forage	38	ND, ND
				Hay	65 (3)	ND, ND
				Grain	105	ND, ND
				Straw	105	ND, ND
Greensburg, KS; 2001 (TCI-01-006-17)	8	Winter Wheat; Blend of 2137/Jagger/2174	0.066	Forage	198	ND, ND
				Hay	227 (10)	ND, ND
				Grain	263	ND, ND
				Straw	263	ND, ND
Eakly, OK; 2001 (TCI-01-006-19)	6/8	Winter Wheat; Jagger	0.067	Forage	164	ND, ND
				Hay	231 (10)	ND, ND
				Grain	257	ND, ND
				Straw	257	ND, ND
Uvalde, TX; 2001 (TCI-01-006-20)	6/8	Winter Wheat; Caudillo	0.067	Forage	66	ND, ND
				Hay	141 (7)	ND, ND
				Grain	177	ND, ND
				Straw	177	ND, ND

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Crop Field Trial - Wheat

TABLE C.3. Residue Data from Wheat Field Trials with *Quizalofop-P-Ethyl*.

Location: City, State; Year (Trial ID)	Zone	Crop; Variety	Total Rate (*lb ai*/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm) [2]
Levelland, TX; 2001 (TCI-01-006-21)	8	Winter Wheat; TAM 105	0.069	Forage	203	ND, ND
				Hay	230 (3)	ND, ND
				Grain	272	ND, ND
				Straw	272	ND, ND
Littlefield, TX; 2001 (TCI-01-006-22)	8	Winter Wheat; TAM 105	0.069	Forage	209	ND, ND
				Hay	223 (6)	ND, ND
				Grain	267	ND, ND
				Straw	267	ND, ND
Payette, ID; 2001 (TCI-01-006-23)	11	Spring Wheat; Penawawa	0.071	Forage	38	ND, ND
				Hay	63 (3)	ND, ND
				Grain	110	ND, ND
				Straw	110	ND, ND
Brookdale, MB; 2001 (TCI-01-006-24)	14	Spring Wheat; AC Cadillac	0.066	Forage	21	ND, ND
				Hay	58 (8)	ND, ND
				Grain	90	ND, ND
				Straw	90	ND, ND
Clanwilliam; MB; 2001 (TCI-01-006-25)	14	Spring Wheat; AC Cadillac	0.066	Forage	30	ND, ND
				Hay	58 (8)	ND, ND
				Grain	115	ND, ND
				Straw	115	ND, ND
Edmonton; AB; 2001 (TCI-01-006-26)	14	Spring Wheat; Barrie	0.069	Forage	54	ND, ND
				Hay	79 (6)	ND, ND
				Grain	118	ND, ND
				Straw	118	ND, ND
Wetaskiwin; AB; 2001 (TCI-01-006-27)	14	Spring Wheat; AC Barrie	0.065	Forage	54	ND, ND
				Hay	84 (8)	ND, ND
				Grain	132	ND, ND
				Straw	132	ND, ND
Wakaw, SK; 2001 (TCI-01-006-28)	14	Spring Wheat; AC Cadillac	0.073	Forage	35	ND, ND
				Hay	60 (10)	ND, ND
				Grain	106	ND, ND
				Straw	106	ND, ND
Minto, MB; 2001 (TCI-01-006-29)	14	Spring Wheat; AC Barrie	0.069	Forage	35	ND, ND
				Hay	75 (10)	ND, ND
				Grain	123	ND, ND
				Straw	123	ND, ND
Lancombe, AB; 2001 (TCI-01-006-30)	14	Spring Wheat; AC Barrie	0.070	Forage	36	ND, ND
				Hay	75 (10)	ND, ND
				Grain	127	ND, ND
				Straw	127	ND, ND
Lancombe, AB; 2001 (TCI-01-006-31)	14	Spring Wheat; AC Barrie	0.068	Forage	42	ND, ND
				Hay	81 (9)	ND, ND
				Grain	126	ND, ND
				Straw	126	ND, ND
Rosthern, SK; 2001	14	Spring Wheat;	0.069	Forage	32	ND, ND

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DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Wheat

TABLE C.3. Residue Data from Wheat Field Trials with Quizalofop-P-Ethyl.

Location: City, State; Year (Trial ID)	*Zone*	*Crop; Variety*	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm) [2]
(TCI-01-006-32)		AC Cadillac		Hay	55 (4)	ND, ND
				Grain	106	ND, ND
				Straw	106	ND, ND
Hepburn, SK; 2001 (TCI-01-006-33)	14	Spring Wheat; Intrepid	0.070	Forage	43	ND, ND
				Hay	60 (4)	ND, ND
				Grain	*98*	ND, ND
				Straw	98	ND, ND

[1] The reported PHI for hay is from last application to cutting; the number of days samples were dried prior to collection is reported in parentheses.
[2] Total quizalofop-ethyl residues = residues of quizalofop-P-ethyl + quizalofop-P acid, converted to quizalofop-P-ethyl-ethyl equivalent.
[3] Less than LOD (0.017 ppm). Residues >LOD and <LOQ (0.05 ppm) are reported in parentheses.

TABLE C.4. Summary of Residue Data from Crop Field Trials with Quizalofop-P-Ethyl.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels [1] (ppm)						
			n	Min.	Max.	HAFT [2]	Median (STMdR) [3]	Mean (STMR) [4]	Std. Dev.
Wheat, forage	0.065-0.073	21-209	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, hay	0.065-0.073	55-231	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, grain	0.065-0.073	90-272	64	<0.05	<0.05	<0.05	<0.025	<0.025	0
Wheat, straw	0.065-0.073	90-272	64	<0.05	<0.05	<0.05	<0.025	<0.025	0

[1] The LOQ was 0.05 ppm and the LOD was 0.017 ppm for all wheat matrices. In calculating the median, mean, and standard deviation, half the LOQ was used for residues reported below the LOQ in Table C.3.
[2] *Highest Average Field Trial.*
[3] Supervised trial median residue
[4] Supervised trial mean residue

D. CONCLUSION

The submitted wheat field trial data reflect the use of a single preplant application of a 0.88 lb/gal EC formulation of quizalofop-P-ethyl at 0.065-0.073 lb ai/A, with a PHI of 21-209 days for wheat forage, 55-231 days for wheat hay, and 90-272 days for wheat grain and straw. An acceptable method was used for quantitation of residues in/on wheat forage, hay, grain, and straw.

E. REFERENCE

DP Barcode: D310869
Subject: PP# 0F6076: Storage Stability DER for Wheat
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885801.Der3

DP Barcode: D310869
Subject: PP# 0F6076: Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885803 and 45885804

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed - Wheat

Primary Evaluator	S. Oonnithan, Biologist. Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006
Peer Reviewer	William Drew, Environmental Scientist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850. The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45885801 Carringer, S. (2002) Magnitude of the Residue of Quizalofop-P-Ethyl and Quizalofop-P in Wheat Raw Agricultural and Processed Commodities: Final Study Report: Lab Project Number: TCI-01-006-01: TCI-01-006-02: TCI-01-006-03. Unpublished study prepared by Morse Laboratories, Inc. 593 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted a wheat processing study from one trial conducted in ID, where a single preplant broadcast application of the 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) was made at 0.35 lb ai/A (5x the field trial application rate). Untreated and bulk treated wheat grain samples were harvested 110 days following application and were processed into bran, flour, germ, middlings, and shorts using simulated commercial processing procedures.

Samples of wheat grain and its processed commodities (bran, flour, germ, middlings, and shorts) were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and its acid metabolite, quizalofop-P) using a high performance liquid chromatography (HPLC) method (Morse Method Meth-147). This method is adequate for data collection based on acceptable method recoveries. The validated limit of quantitation (LOQ) was 0.05 ppm for wheat grain and its processed commodities, and the defined limit of detection (LOD) was 0.017 ppm for all wheat matrices. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage duration of the study samples from collection/processing to analysis was 1.7 months for wheat grain and <1.0 month for the processed wheat commodities. Adequate

storage stability data submitted in conjunction with the wheat field trials (refer to the 860.1380 DER1 for MRID 45885801), support the storage conditions and intervals of wheat grain (RAC) samples from the processing study. Storage stability data are not required for the wheat processed commodities because samples were stored frozen prior to analysis and were analyzed within one month of processing.

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on wheat grain. Residues of total quizalofop-P-ethyl were also less than the LOQ in processed wheat bran, flour, germ, middlings, and shorts. Therefore, processing factors were not calculated.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the wheat processed commodity residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document [D310869].

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

TABLE A.1. Test Compound Nomenclature.

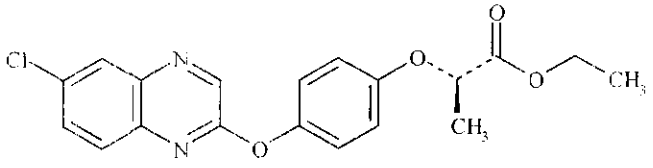
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

Details of the use pattern are summarized in Table B.1.1. In one trial, a single preplant broadcast application of the 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) was made at 0.35 lb ai/A (5x the field trial application rate). Untreated and bulk treated wheat grain samples were harvested 110 days following application. The proposed label did not specify a preharvest interval (PHI) for wheat grain (RAC).

TABLE B.1.1. Study Use Pattern

Location: City, State; Year (Trial ID)	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume [2] (GPA)	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Payette, ID; 2003 (TCI-01-006-23)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	20.7	0.35	NA	0.35 (5x)	Crop Oil [4]

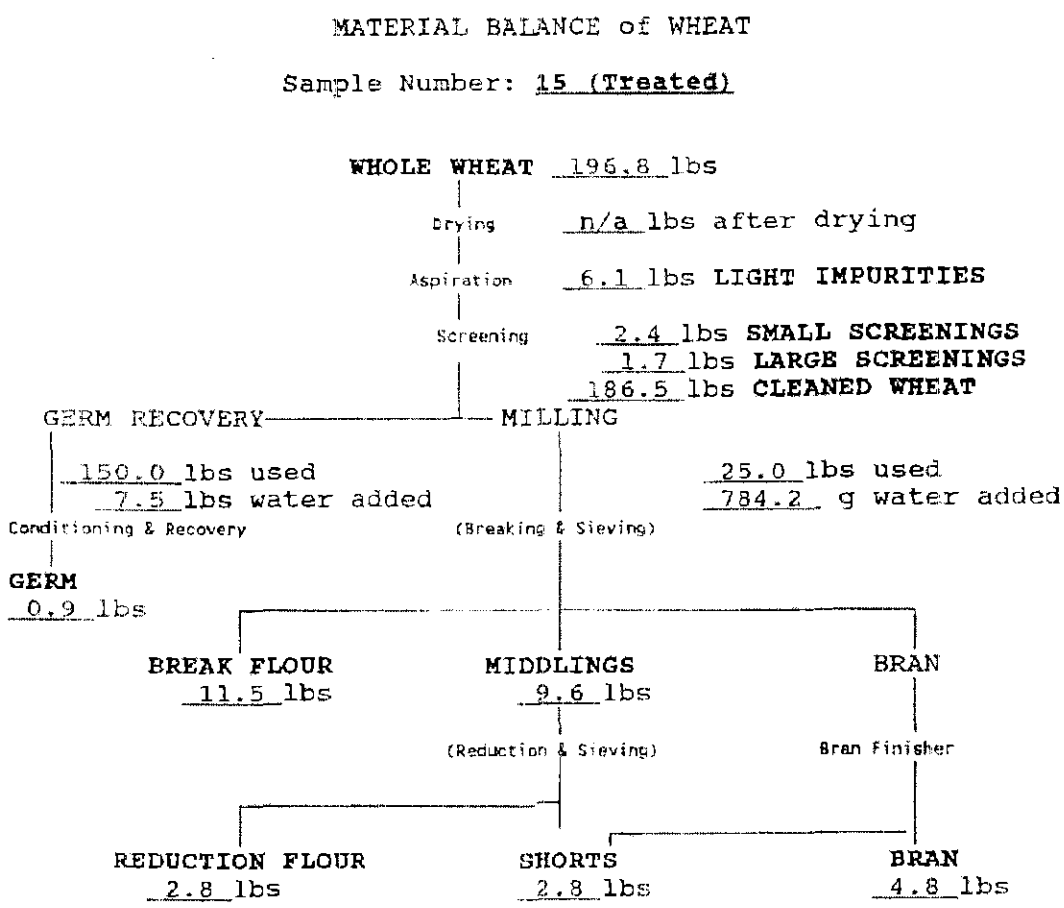
[1] End-use Product; EPA Reg. No. 352-541
[2] Gallons per acre
[3] Retreatment Interval; NA = Not applicable
[4] Petroleum based crop oil; added to spray mixture at 1% v/v.

B.2. Sample Collection, Handling, and Processing Procedures

Bulk wheat grain samples were collected, frozen within 2.25 hours of collection, and kept in frozen storage until sample shipment to Texas A. & M. Food Protein Research & Development Center (Bryan, TX) for processing. Samples were maintained frozen (≤ -12 °C) at Food Protein Research & Development Center until processing. Grain was processed within 25-26 days of harvest into bran, flour, germ, middlings, and shorts using simulated commercial processing procedures. The RAC and processed commodities were stored frozen (≤ -12 °C) at the Food Protein Research & Development Center, and shipped frozen to Morse Laboratories (Sacramento, CA) for residue analysis. Samples were stored frozen (-20 ± 5 °C) at the analytical laboratory until analysis.

The wheat processing procedures are summarized below in Figure 1, which was copied without alteration from MRID 45885801.

FIGURE 1. Processing Flowchart for Wheat



B.3. Analytical Methodology

Samples of wheat grain and its processed commodities (bran, flour, germ, middlings, and shorts) were analyzed for residues of total quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using the HPLC method (Morse Method Meth-147). A brief description of the method is included below; for a complete description, refer to the DER for MRID 45885803.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC). The GPC eluate was concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. The validated LOQ was 0.05 ppm for wheat grain and its processed commodities, and the defined

LOD was 0.017 ppm for all matrices. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

C. RESULTS AND DISCUSSION

Wheat grain was harvested 110 days following a single preplant broadcast application of the 0.88 lb/gal EC formulation at 0.35 lb ai/A (5x the field trial application rate). Wheat grain was processed into bran, flour, germ, middlings, and shorts using simulated commercial processing procedures.

Sample storage durations and conditions are summarized in Table C.1. Wheat and processed wheat commodities were stored frozen following harvest/processing until analysis. The maximum storage interval of the study samples from collection/processing to analysis was 1.7 months for wheat grain and <1.0 month for the processed wheat commodities. To support sample storage conditions and durations, the petitioner included storage stability data on wheat matrices with the field trial submission (refer to the 860.1380 DER1 for MRID 45885801). These data demonstrate that residues of quizalofop-P-ethyl and quizalofop-P are relatively stable in/on wheat grain stored frozen for ~13 months, and support the storage conditions and durations of wheat grain (RAC) samples from the processing study. Storage stability data are not required for the wheat processed commodities because samples were stored frozen prior to analysis and were analyzed within one month of processing.

TABLE C.1. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability [2]
Wheat grain (RAC)	-20 ± 5	51 days (1.7 months)	Quizalofop-P-ethyl and quizalofop-P are relatively stable in/on fortified wheat forage and grain stored frozen for 12.7 months, and wheat hay and straw stored frozen for 11.2 months.
Wheat processed commodities (bran, flour, germ, middlings, and shorts)	Processing: ≤ -12 Analysis: -20 ± 5	25-27 days (<1.0 month)	None required.

[1] Actual storage duration from harvest to analysis for RAC and processing to analysis for processed commodities; samples were processed within 25-26 days of harvest and analyzed within 3-8 days of extraction.
[2] D310869 Storage Stability Der3 for MRID 45885801.

Concurrent recovery data from the wheat processing study are presented in Table C.2. Samples of wheat grain and its processed commodities (bran, flour, germ, middlings, and shorts) were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using an HPLC method (Morse Method Meth-147). The method is adequate for data collection based on acceptable concurrent method recovery data; overall recoveries ranged 72-98% for grain fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-0.20 ppm, and 79-101% for flour, 71-88% for middlings, 76-86% for bran, 73-85% for germ, and 68-82% for shorts fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-0.10 ppm. The validated LOQ was 0.05 ppm for wheat grain and its processed commodities. Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on one sample each of untreated wheat grain and its processed commodities.

TABLE C.2 Summary of Concurrent Recoveries of Quizalofop-P-Ethyl and Quizalofop-P from Wheat Matrices.					
Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean [std dev] (%)
Wheat, grain (RAC)	Quizalofop-P-ethyl	0.05	9	72, 75, 87, 88, 90, 91, 95, 96, 98	88 [7]
		0.1	4	84, 88, 91, 91	
		0.2	1	88	
	Quizalofop-P	0.05	8	74, 78, 80, 80, 82, 82, 92, 94	82 [6]
		0.1	2	80, 81	
		0.2	1	83	
Wheat, bran	Quizalofop-P	0.05	2	76, 81	80 [5]
		0.10	2	76, 86	
Wheat, flour	Quizalofop-P-ethyl	0.05	2	79, 101	88 [9]
		0.10	2	85, 88	
Wheat, germ	Quizalofop-P	0.05	2	73, 85	77 [6]
		0.10	2	73, 78	
Wheat, middlings	Quizalofop-P-ethyl	0.05	2	71, 83	81 [7]
		0.10	2	83, 88	
Wheat, shorts	Quizalofop-P	0.05	2	75, 82	76 [6]
		0.10	2	68, 80	

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on wheat grain harvested 110 days following a single preplant broadcast application of the 0.88 lb/gal EC formulation at 0.35 lb ai/A. Residues of total quizalofop-P-ethyl were also less than the method LOQ in processed wheat bran, flour, germ, middlings, and shorts. Processing factors could not be calculated because residues were below the LOQ in/on the RAC and the processed commodities.

TABLE C.3. Residue Data from Wheat Processing Study with Quizalofop-P-Ethyl.					
RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Total Quizalofop-P-Ethyl Residues [1] (ppm)	Processing Factor [2]
Wheat	Grain (RAC)	0.35	110	ND, ND	---
	Bran			ND, ND	NC
	Flour			ND, ND	NC
	Germ			ND, ND	NC
	Middlings			ND, ND	NC
	Shorts			ND, ND	NC

[1] Nondetectable (below the method LOD of <0.017 ppm).
[2] Not calculated because residues were nondetectable in both the RAC and the processed fraction.

D. CONCLUSION

Processing factors for total quizalofop-P-ethyl in wheat bran, flour, germ, middlings, and shorts were not calculated because residues were nondetectable in both the RAC (wheat grain) and all wheat processed commodities. An acceptable method was used for quantitation of residues in/on wheat grain and its processed commodities.

E. REFERENCES

DP Barcode: D310869
Subject: PP# 0F6076: Storage Stability DER for Wheat
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885801.Der3

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.3/OPPTS 860.1380/OECD IIA 6.1.1 and IIIA 8.1.1
Storage Stability – Wheat Commodities

Primary Evaluator S. Oonnithan, Biologist — Date: June 13, 2006
Registration Action Branch 2
Health Effects Division (7509 P)

Peer Reviewer William Drew, Environmental Scientist — Date: June 13, 2006
Registration Action Branch 2
Health Effects Division (7509 P)

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850. The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45885801 Carringer, S. (2002) Magnitude of the Residue of Quizalofop-P-Ethyl and Quizalofop-P in Wheat Raw Agricultural and Processed Commodities: Final Study Report: Lab Project Number: TCI-01-006-01: TCI-01-006-02: TCI-01-006-03. Unpublished study prepared by Morse Laboratories, Inc. 593 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted the results of a storage stability study with quizalofop-P-ethyl and its acid metabolite quizalofop-P in wheat matrices. Separate untreated samples of wheat forage, hay, grain and straw were fortified with standards of quizalofop-P-ethyl or quizalofop-P at 2.5 ppm were placed in frozen storage at ca. -20 °C and analyzed at storage durations of 0, 32-39, and 341-386 days.

Samples of the wheat matrices were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using a high performance liquid chromatography (HPLC) method (Morse Method Meth-147). This method is adequate for data collection based on acceptable method recoveries. The validated LOQ was 0.05 ppm for wheat forage, hay, grain and straw.

The results indicate that under the conditions of the study, residues of quizalofop-P-ethyl, and quizalofop-P are stable in/on wheat forage, and grain for up to 12.7 months, wheat hay for up to 11.3 months, and wheat straw for up to 11.2 months.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the storage stability data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document D310869.

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

TABLE A.1. Test Compound Nomenclature.

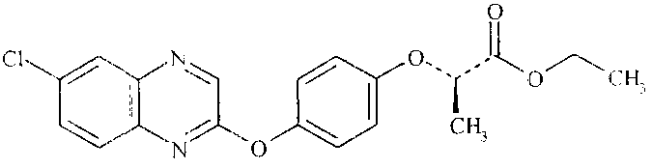
Chemical structure	
Common name	*Quizalofop-P-ethyl*
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Sample Handling and Preparation

Separate samples of homogenized wheat forage, hay, grain and straw were fortified with quizalofop-P-ethyl or quizalofop-P at 2.5 ppm. The quizalofop-P-ethyl fortification standards were prepared in acetonitrile (ACN) and the quizalofop-P fortification standards were prepared in ACN with 0.2% acetic acid. The fortification standards were considered to be stable for 48 days. Fortified and unfortified samples were stored frozen (<-20 ± 5 °C) and analyzed at 0-, 32- to 39-, and 341- to 386-day storage intervals.

B.2. Analytical Methodology

Samples of the wheat matrices were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using the HPLC method (Morse Method Meth-147). For a complete description of the method, refer to the D310869, DER for MRIDs 45885803 and 45885804.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC); the hexane fractions of wheat hay and straw were cleaned up by silica solid-phase extraction prior to GPC cleanup. The GPC eluate was concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl or quizalofop-P equivalents using molecular weight conversion factors of 1.917 and 1.773, respectively. The defined limit of detection (LOD) was 0.017 ppm for all matrices and the validated limit of quantitation (LOQ) was 0.05 ppm for wheat forage, hay, grain and straw.

C. RESULTS AND DISCUSSION

Based on the concurrent method recovery data (see Table C.1), the HPLC method (Morse Method Meth-147) is adequate for the determination of residues of quizalofop-P-ethyl and quizalofop-P in wheat and wheat commodities. All concurrent recoveries ranged 71-95% and are acceptable. Apparent residues of quizalofop-P-ethyl and quizalofop-P were less than the LOQ (<0.05 ppm) in the control samples for wheat.

TABLE C.1. Summary of Concurrent Recoveries of Quizalofop-P-Ethyl and Quizalofop-P from Wheat Matrices.

Matrix	Analyte	Spike Level (ppm)	Storage Interval (days)	Sample Size (n)	Recoveries (%)	Mean (%)
Wheat, forage	Quizalofop-P-ethyl	2.5	0	3	83, 84, 95	87
			35	2	81, 88	85
			385	2	88, 91	90
	Quizalofop-P	2.5	0	3	71, 76, 80	76
			35	2	76, 77	77
			385	2	81, 83	82
Wheat, hay	Quizalofop-P-ethyl	2.5	0	3	89, 92, 94	92
			35	2	83, 84	84
			343	2	86, 88	87
	Quizalofop-P	2.5	0	3	80, 84, 87	84
			35	2	75, 76	76
			343	2	81, 81	81
Wheat, grain	Quizalofop-P-ethyl	2.5	0	3	84, 86, 90	87
			32	2	84, 88	86
			386	2	88, 89	89
	Quizalofop-P	2.5	0	3	72, 77, 79	76
			32	2	80, 80	80
			386	2	81, 83	82
Wheat, straw	Quizalofop-P-ethyl	2.5	0	3	82, 84, 91	86
			39	2	82, 84	83
			341	2	83, 87	85
	Quizalofop-P	2.5	0	3	78, 79, 80	79
			39	2	71, 76	74
			341	2	77, 79	78

Based on the results of storage stability study (Table C.2), residues of quizalofop-P-ethyl and quizalofop-P are relatively stable in/on wheat forage and grain stored frozen for up to 385 days (12.7 months), wheat hay stored frozen for up to 343 days (11.3 months), and wheat straw stored frozen for up to 341 days (11.2 months).

TABLE C.2. Stability of Quizalofop-P-Ethyl and Quizalofop-P from Wheat Matrices Following Storage at ca. -20 °C.

Commodity	Analyte	Spike Level (ppm)	Storage Interval [1] (days)	Recovered Residues (ppm)	Mean Recovered Residues (ppm)	Mean Recovery (%)	Corrected Recovery [2] %
Wheat, forage	Quizalofop-P-Ethyl	2.5	0 (5)	2.08, 2.09, 2.38	2.18	87	---
			35 (3)	2.10, 2.13	2.12	85	100
			385 (8)	2.35, 2.39	2.37	95	106
	Quizalofop-P	2.5	0 (6)	1.78, 1.90, 1.99	1.89	76	---
			35 (3)	2.01, 2.21	2.11	84	109
			385 (9)	2.19, 2.27	2.23	89	109
Wheat, hay	Quizalofop-P-Ethyl	2.5	0 (3)	2.23, 2.31, 2.35	2.30	92	---
			35 (8)	2.14, 2.18	2.16	86	102
			343 (8)	2.34, 2.37	2.36	94	108
	Quizalofop-P	2.5	0 (4)	2.01, 2.10, 2.18	2.10	84	---
			35 (8)	1.96, 2.01	1.99	80	105
			343 (8)	2.02, 2.05	2.04	82	101
Wheat, grain	Quizalofop-P-Ethyl	2.5	0 (4)	2.10, 2.16, 2.26	2.17	87	---
			32 (2)	2.12, 2.16	2.14	86	100
			386 (6)	2.34, 2.38	2.36	94	106
	Quizalofop-P	2.5	0 (4)	1.81, 1.93, 1.98	1.91	76	---
			32 (2)	1.92, 1.93	1.93	77	96
			386 (6)	2.1, 2.2	2.2	88	107
Wheat, straw	Quizalofop-P-Ethyl	2.5	0 (8)	2.06, 2.09, 2.28	2.14	86	---
			39 (8)	2.16, 2.21	2.19	88	106
			341 (7)	2.31, 2.31	2.31	92	108
	Quizalofop-P	2.5	0 (8)	1.94, 1.98, 1.99	1.97	79	---
			39 (8)	1.91, 1.99	1.95	78	105
			341 (7)	2.12, 2.14	2.13	85	109

[1] The storage duration from fortification to extraction; the days from extraction to analysis are reported in parentheses.
[2] Corrected for mean concurrent recovery (see TABLE C.1.).

D. CONCLUSION

The submitted storage stability results are adequately to demonstrate the stability of quizalofop-P-ethyl and quizalofop-P residues in/on wheat forage and grain stored frozen for 12.7 months, wheat hay stored frozen for 11.3 months, and wheat straw stored frozen for 11.2 months. An acceptable method was used for the quantitation of residues in wheat forage, hay, grain, and straw.

E. REFERENCES

DP Barcode: D310869
Subject: PP# 0F6076: DER for the Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities.
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885803, 45858504

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/128709/Nissan Chemical Industries, Ltd./33906
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1. 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Barley

Primary Evaluator	S. Oonnithan, Biologist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006
Peer Reviewer	William Drew, Environmental Scientist Registration Action Branch 2 Health Effects Division (7509 P)	Date: June 13, 2006

This Data Evaluation Record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 03/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

45885802 Carringer, S. (2002) Magnitude of the Residue of Quizalofop-P-Ethyl and Quizalofop-P in Barley Raw Agricultural Commodities: Final Study Report: Lab Project Number: TCI-01-007-08: TCI-01-007-09: TCI-01-007-10. Unpublished study prepared by Morse Laboratories, Inc. 377 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted field trial data for quizalofop-P-ethyl on barley. A total of twenty-five trials were conducted in the U.S. and Canada during the 2001 and 2002 growing season. The U. S. trials were conducted in Zones 1 (NY; 1 trial), 5 (KS and ND; 2 trials), 7 (NE and ND; 2 trials), 9 (UT; 1 trial), 10 (CA; 1 trial), and 11 (ID and WA; 2 trials). The Canadian trials were conducted in Zones 5 (ON; 1 trial), 5B (QC; 1 trial), 7 (SK; 1 trial), 7A (AB; 1 trial), and 14 (AB, MB, and SK; 12 trials). All field trials were conducted on spring barley, except for one which was conducted on fall barley.

At each test location, a single preplant broadcast application of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl was made to the soil surface at ~0.068 lb ai/A on or the day before planting. All applications were made using ground equipment in spray volumes of 5.0-20.5 gal/A. Samples of barley hay were harvested 48-219 days after application and dried in the field for 1-12 days, and samples of mature barley grain and straw were harvested 90-255 days after application.

Samples of barley matrices were analyzed for residues of total quizalofop-P-ethyl (quizalofop-P-ethyl and its acid metabolite, quizalofop-P) using a high performance liquid chromatography (HPLC) method (Morse Method Meth-147). This method is adequate for data collection based on acceptable method recoveries. The validated limit of quantitation (LOQ) was 0.05 ppm and

the defined limit of detection (LOD) was 0.017 ppm for all barley matrices. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

The maximum storage durations of samples from harvest to analysis were 7.5 months for barley hay, 6.7 months for barley grain, and 7.3 months for barley straw. Storage stability data are available for wheat hay, grain, and straw which may be translated to support the storage conditions and durations of samples from the submitted barley field trials.

Residues of total quizalofop-P-ethyl were less than the method LOQ (<0.05 ppm) in/on all samples of barley hay harvested 48-219 days after application, and all samples of barley grain and straw harvested 90-255 days after application.

No residue decline study was included in the submission; these data are not required because application was made prior to crop emergence.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the U. S. EPA Residue Chemistry Summary Document, DP Barcode D310869.

COMPLIANCE

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide used for the control of annual, and perennial grasses in cropped, and non-cropped land areas, and is applied as preplant, preemergence, or postemergence. Chemically, quizalofop-P-ethyl is a racemic mixture of R and S enantiomers, and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties of quizalofop-P-ethyl are summarized in Tables A.1 and A. 2.

TABLE A.1. Test Compound Nomenclature.

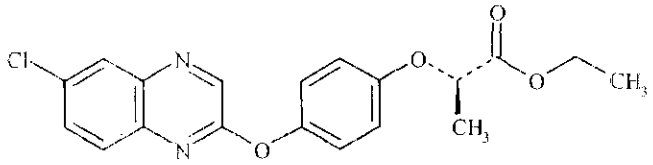
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.

Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C acetone 650 benzene 680 carbon disulfide 660 chloroform 1350 cyclohexanone 440 dichloromethane 1970 dimethyl sulfoxide 200 ethanol 22 n-hexane 5 methanol 22 tetrahydrofuran 1160 toluene 430 xylene 360	
Vapor pressure	8.3 x 10^{-0} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year (Trial ID No.)	Soil characteristics [1]			
	Type	%OM [2]	pH	CEC [3]
North Rose, NY; 2001 (TCI-01-007-01)	Sand	N/A [4]		
Andale, KS; 2001 (TCI-01-007-02)	Silt loam	N/A		
New Rockford, ND; 2001 (TCI-01-007-03)	Loam	N/A		
Sheffield, ON; 2001 (TCI-01-007-04)	Silt loam	N/A		
St. Paul-D'Abbotsford, QC (TCI-01-007-05)	Loamy sand	N/A		
Velva, ND; 2001 (TCI-01-007-06)	Loam	N/A		
Grand Island, NE; 2001 (TCI-01-007-07)	Silt loam	N/A		
Delisle, SK; 2001 (TCI-01-007-08)	Loam	N/A		
Taber, AB; 2001 (TCI-01-007-09)	Loam	N/A		
Smithfield, UT; 2001 (TCI-01-007-10)	Silty clay loam	N/A		
Porterville, CA; 2001 (TCI-01-007-11)	Sandy loam	N/A		
Payette, ID; 2001 (TCI-01-007-12)	Loam	N/A		
Ephrata, WA; 2001 (TCI-01-007-13)	Sandy loam	N/A		
Blaine Lake, SK; 2001 (TCI-01-007-14)	Sandy loam	N/A		
Wakaw, SK; 2001 (TCI-01-007-15)	Silty loam/ loam	N/A		
Brookdale, MB; 2001 (TCI-01-007-16)	Loam/ clay loam	N/A		
Ianwilliam, MB (TCI-01-007-17)	Clay loam	N/A		
Edmonton, AB; 2001 (TCI-01-007-18)	Clay loam	N/A		
Wetaskiwin, AB; 2001 (TCI-01-007-19)	Loam	N/A		
Minto, MB; 2001 (TCI-01-007-20)	Loam/ clay loam	N/A		
Boissevain, MB; 2001 (TCI-01-007-21)	Loam/ clay loam	N/A		
Lancombe, AB; 2001 (TCI-01-007-22)	Silt loam	N/A		
Lancombe, AB; 2001 (TCI-01-007-23)	Silt loam	N/A		
Rosthern, SK; 2001 (TCI-01-007-24)	Clay/ loam	N/A		
Hepburn, SK; 2001 (TCI-01-007-25)	Clay/ loam	N/A		

[1] These parameters are not applicable since they do not affect the proposed use pattern for this chemical.
[2] Organic matter
[3] Cation exchange capacity
[4] Not applicable

The study site details are summarized in Table B.1.1. The actual temperature recordings were within average historical values for the residue study period for all trials. The actual rainfall average was below the historical rainfall average at many sites; however, this did not have a significant impact on growth and development at any sites with the exception of two trials (-18 and -19) in which the crop was stressed due to drought conditions and one trial (-25) where the crop was rated as fair. Irrigation was used to supplement rainfall in 5 trials.

The use pattern employed in the study and the geographical locations are summarized in Table B.1.2. At each test location, a single preplant broadcast application of a 0.88 lb/gal emulsifiable concentrate (EC) formulation of quizalofop-P-ethyl (Assure II; EPA Reg. No. 352-541) was

made to the soil surface at ~0.068 lb ai/A on or the day before planting. All applications were made using ground equipment in volumes of 5.0-20.5 gal/A, with an adjuvant (petroleum-based crop oil concentrate) added to the spray mixture. The label did not propose a preharvest interval (PHI) for the barley grain (RAC).

TABLE B.1.2. Study Use Pattern.

Location (City, State; Year) Trial ID	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
North Rose, NY; 2001 (TCI-01-007-01)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	18.0	0.068	NA [4]	0.068	Crop Oil [5]
Andale, KS; 2001 (TCI-01-007-02)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.1	0.068	NA	0.068	Crop Oil
New Rockford, ND; 2001 (TCI-01-007-03)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.0	0.068	NA	0.068	Crop Oil
Sheffield, ON; 2001 (TCI-01-007-04)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	14.6	0.069	NA	0.069	Crop Oil
St. Paul-D'Abbotsford, QC (TCI-01-007-05)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	19.5	0.069	NA	0.069	Crop Oil
Velva, ND; 2001 (TCI-01-007-06)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.1	0.068	NA	0.068	Crop Oil
Grand Island, NE; 2001 (TCI-01-007-07)	0.88 lb/gal EC	Preplant broadcast; on the day of planting	5.0	0.068	NA	0.068	Crop Oil
Delisle, SK; 2001 (TCI-01-007-08)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	12.1	0.068	NA	0.068	Crop Oil
Taber, AB; 2001 (TCI-01-007-09)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.5	0.067	NA	0.067	Crop Oil
Smithfield, UT; 2001 (TCI-01-007-10)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	15.7	0.070	NA	0.070	Crop Oil
Porterville, CA; 2001 (TCI-01-007-11)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.0	0.069	NA	0.069	Crop Oil
Payette, ID; 2001 (TCI-01-007-12)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	20.5	0.070	NA	0.070	Crop Oil
Ephrata, WA; 2001 (TCI-01-007-13)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.3	0.069	NA	0.069	Crop Oil
Blaine Lake, SK; 2001 (TCI-01-007-14)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.9	0.068	NA	0.068	Crop Oil
Wakaw, SK; 2001 (TCI-01-007-15)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	12.1	0.069	NA	0.069	Crop Oil
Brookdale, MB; 2001 (TCI-01-007-16)	0.88 lb/gal EC	Preplant broadcast; on the day of planting	11.8	0.066	NA	0.066	Crop Oil
Clanwilliam, MB (TCI-01-007-17)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	12.1	0.069	NA	0.069	Crop Oil
Edmonton, AB; 2001 (TCI-01-007-18)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.6	0.067	NA	0.067	Crop Oil
Wetaskiwin, AB; 2001 (TCI-01-007-19)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	11.8	0.067	NA	0.067	Crop Oil
Minto, MB; 2001 (TCI-01-007-20)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	5.1	0.069	NA	0.069	Crop Oil
Boissevain, MB; 2001 (TCI-01-007-21)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.9	0.069	NA	0.069	Crop Oil

TABLE B.1.2. Study Use Pattern.

Location (City, State; Year Trial ID	EP [1]	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume (GPA) [2]	Rate (lb ai/A)	RTI [3] (days)	Total Rate (lb ai/A)	
Lancombe, AB; 2001 (TCI-01-007-22)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.8	0.070	NA	0.070	Crop Oil
Lancombe, AB; 2001 (TCI-01-007-23)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.5	0.067	NA	0.067	Crop Oil
Rosthern, SK; 2001 (TCI-01-007-24)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.7	0.069	NA	0.069	Crop Oil
Hepburn, SK; 2001 (TCI-01-007-25)	0.88 lb/gal EC	Preplant broadcast; one day prior to planting	10.5	0.068	NA	0.068	Crop Oil

[1] End-use Product; EPA Reg. No. 352-541
[2] Gallons per acre
[3] Retreatment interval
[4] Not applicable
[5] Petroleum based crop oil; added to all spray mixtures at 1% v/v.

The geographical locations are summarized in Table B.1.3.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Barley		
	Submitted	Requested [1]	
		Canada	U.S.
1	1		1 (1) [2]
1A			
2			1 (1) [2]
3			
4			
5	3	1	3 (2)
5A			
5B	1	1	
6			
7	3	2	4 (3)
7A	1		
8			
9	1		1 (1)
10	1		1 (1)
11	2		2 (1)
12			
13			
14	12	12	
15			
16			
17			
18			
19			
20			
21			

TABLE B.1.3. Trial Numbers and Geographical Locations.			
NAFTA Growing Zones	Barley		
	Submitted	Requested [1]	
		Canada	U.S.
Total	25	16	12 (9)

[1] As per OPPTS 860.1500, Tables 1 and 5 and Directive 98-02; Section 9 for barley as an individual crop; the values presented in parentheses represent a 25% reduction in the number of trials required, due to pesticide use resulting in no quantifiable residues.
[2] One trial is required in either Zone 1 or Zone 2.

B.2. Sample Collection, Handling, and Preparation

Single untreated and duplicate treated samples of the barley matrices were collected by hand or using a thresher/combine from each field trial. Barley hay was harvested at the early flowering (boot) to soft dough growth stage (48-219 days after application) and dried in the field for 1-12 days. Mature barley grain and straw were harvested 90-255 days after application. All samples were frozen within ~6 hours of sampling and shipped frozen to the Morse Laboratories, Inc. (Sacramento, CA) for residue analysis. Samples were stored frozen (-20 ± 5 °C) at the analytical laboratory until analysis; samples were homogenized in the presence of dry ice prior to analysis.

B.3. Analytical Methodology

Samples of barley hay, grain, and straw were analyzed for residues of quizalofop-P-ethyl (the total of the parent quizalofop-P-ethyl and its acid metabolite quizalofop-P) using the HPLC method (Morse Method Meth-147). A brief description of the method is included below; for a complete description of the method, refer to the D310869 DER for Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities, MRIDs 45885803 and 45858504.

Briefly, samples were refluxed with methanolic potassium hydroxide to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution was acidified and partitioned with hexane to extract the MeCHQ and the hexane fraction was cleaned up by gel permeation chromatography (GPC); the hexane fractions of barley hay and straw were cleaned up by silica solid-phase extraction prior to GPC cleanup. The GPC eluate was concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Residues were reported as quizalofop-P-ethyl equivalents using a molecular weight conversion factor of 1.917. We note that based on the hydrolysis procedures of Morse Method Meth-147, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop. The validated LOQ was 0.05 ppm for barley hay, grain and straw, and the defined LOD was 0.017 ppm for all matrices.

We note that the petitioner calculated LOQ and LOD values for each barley matrix using the standard deviation of method recoveries at the LOQ. But, for reporting the results, the petitioner used the validated LOQ value of 0.05 ppm (higher than calculated LOQs) and the defined LOD value of 0.017 ppm (higher than calculated LODs).

Concurrent method validation data were collected for the barley matrices (see Table C.2), including at the defined LOD level. Recoveries at the LOD fortification level were 66-122% in barley hay, grain and straw. These data were collected to verify the LOD and are not included with the concurrent method recovery data in Table C.2.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.1. The maximum storage duration of samples from harvest to analysis were 228 days (7.5 months) for barley hay, 203 days (6.7 months) for barley grain, and 222 days (7.3 months) for barley straw. To support the storage conditions and durations of samples from the barley field trials, wheat storage stability data (D310869, DER for Storage Stability - Wheat, MRID 45885801) may be translated. The wheat storage stability study demonstrate that residues of quizalofop-P-ethyl and quizalofop-P are stable in/on wheat forage, hay, grain, and straw stored frozen for ~11-13 months.

TABLE C.1. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability [2]
Barley, hay	-20 ± 5	83-228 days (2.7-7.5 months)	Quizalofop-P-ethyl and quizalofop-P are stable in/on fortified wheat forage and grain stored frozen for 12.7 months, and wheat hay and straw stored frozen for 11.2 months.
Barley, grain		45-203 days (1.5-6.7 months)	
Barley, straw		47-222 days (1.5-7.3 months)	

[1] Storage duration from collection to analysis; samples were analyzed within 3-14 days of extraction.
[2] Translated from wheat - D310869 DER for the Storage stability study, MRID 45885801.

Concurrent method recovery data are presented in Table C.2. Barley matrices were analyzed for residues of quizalofop-P-ethyl and quizalofop-P using an HPLC method (Morse Method Meth-147). The method is adequate for data collection based on acceptable concurrent method recovery data. Recoveries ranged 70-93% for hay, 71-99% for grain, and 70-93% for straw fortified with quizalofop-P-ethyl or quizalofop-P at 0.05-0.20 ppm. The validated LOQ was 0.05 ppm. Apparent residues of total quizalofop-P-ethyl were below the LOQ in/on all samples of untreated hay, grain, and straw, except for one untreated straw sample which bore residues at 0.095 ppm. The petitioner stated that these residues were likely due to laboratory contamination.

TABLE C.2. Summary of Concurrent Recoveries of Quizalofop-P-Ethyl and Quizalofop-P from Barley Matrices.

Matrix	Analyte	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean [Std. Dev.] (%)
Barley, hay	Quizalofop-P-ethyl	0.05	7	75, 79, 81, 90, 92, 93, 93	85 [6]
		0.1	2	82, 87	
		0.2	1	82	
	Quizalofop-P	0.05	7	70, 73, 74, 78, 82, 87, 88	78 [7]
		0.1	2	71, 73	
		0.2	1	87	
Barley, grain	Quizalofop-P-ethyl	0.05	7	76, 78, 78, 83, 83, 96, 99	85 [8]
		0.1	2	80, 90	
		0.2	1	86	
	Quizalofop-P	0.05	7	71, 74, 76, 76, 81, 82, 88	78 [5]
		0.1	1	77	
		0.2	1	81	
Barley, straw	Quizalofop-P-ethyl	0.05	7	72, 74, 77, 85, 91, 92, 93	84 [8]
		0.1	2	78, 81	
		0.2	1	93	
	Quizalofop-P	0.05	7	70, 73, 75, 83, 85, 92, 92	79 [9]
		0.1	2	71, 75	
		0.2	1	70	

Residue data from the barley field trials are reported in Table C.3 and a summary of residue data for barley hay, grain, and straw is presented in Table C.4. Following a single preplant application of the 0.88 lb/gal EC formulation at 0.066-0.070 lb ai/A, residues of total quizalofop-P-ethyl were less than the LOQ in/on all samples of barley hay harvested 48-219 days after application, and barley grain and straw harvested 90-255 days after application.

TABLE C.3. *Residue Data from* Barley Field Trials with Quizalofop-P-Ethyl.

Trial ID (City, State; Year)	Zone	Crop; Variety	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm)
North Rose, NY; 2001 (TCI-01-007-01)	1	Barley; AC Stephen	0.068	Hay	69 (2)	ND, ND [3]
				Grain	93	ND, ND
				Straw	93	ND, ND
Andale, KS; 2001 (TCI-01-007-02)	5	Barley; R. Hitchcock (fall barley)	0.068	Hay	219 (10)	ND, ND
				Grain	255	ND, ND
				Straw	255	ND, ND
New Rockford, ND; 2001 (TCI-01-007-03)	5	Barley; Stander	0.068	Hay	58 (4)	ND, ND
				Grain	92	ND, ND
				Straw	92	ND, ND
Sheffield, ON; 2001 (TCI-01-007-04)	5	Barley; Chapais	0.069	Hay	64 (8)	ND, ND
				Grain	93	ND, ND
				Straw	93	ND, ND
St. Paul-D'Abbotsford, QC	5B	Barley; Chapais	0.069	Hay	48 (1)	ND, ND

TABLE C.3. Residue Data from Barley Field Trials with Quizalofop-P-Ethyl.

Trial ID (City, State; Year)	Zone	Crop; Variety	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm)
(TCI-01-007-05)				Grain	98	ND, ND
				Straw	98	ND, ND
Velva, ND; 2001 (TCI-01-007-06)	7	Barley; Robust	0.068	Hay	65 (1)	ND, ND
				Grain	96	ND, ND
				Straw	96	ND, ND
Grand Island, NE; 2001 (TCI-01-007-07)	7	Barley; Robust	0.068	Hay	63 (2)	ND, ND
				Grain	96	ND, ND
				Straw	96	ND, ND
Delisle, SK; 2001 (TCI-01-007-08)	7	Barley; Harrington	0.068	Hay	64 (7)	ND, ND
				Grain	103	ND, ND
				Straw	103	ND, ND
Taber, AB; 2001 (TCI-01-007-09)	7A	Barley; Stander	0.067	Hay	65 (3)	ND, ND
				Grain	101	ND, ND
				Straw	101	ND, ND
Smithfield, UT; 2001 (TCI-01-007-10)	9	Barley; Baronesse	0.070	Hay	71 (3)	ND, ND
				Grain	104	ND, ND
				Straw	104	ND, ND
Porterville, CA; 2001 (TCI-01-007-11)	10	Barley; Solum	0.069	Hay	64 (12)	ND, ND
				Grain	104	ND, ND
				Straw	104	ND, ND
Payette, ID; 2001 (TCI-01-007-12)	11	Barley; Baroness	0.070	Hay	63 (3)	ND, ND
				Grain	113	ND, ND
				Straw	113	ND, ND
Ephrata, WA; 2001 (TCI-01-007-13)	11	Barley; Baronesse	0.069	Hay	71 (3)	ND, ND
				Grain	122	ND, ND
				Straw	122	ND, ND
Blaine Lake, SK; 2001 (TCI-01-007-14)	14	Barley; Harrington	0.068	Hay	56 (8)	ND, ND
				Grain	116	ND, ND
				Straw	116	ND, ND
Wakaw, SK; 2001 (TCI-01-007-15)	14	Barley; Harrington	0.069	Hay	60 (10)	ND, ND
				Grain	106	ND, ND
				Straw	106	ND, ND
Brookdale, MB; 2001 (TCI-01-007-16)	14	Barley; Robust	0.066	Hay	58 (8)	ND, ND
				Grain	90	ND, ND
				Straw	90	ND, ND
Clanwilliam, MB (TCI-01-007-17)	14	Barley; Robust	0.069	Hay	57 (8)	ND, ND
				Grain	114	ND, ND
				Straw	114	ND, ND
Edmonton, AB; 2001 (TCI-01-007-18)	14	Barley; Mahigan	0.067	Hay	79 (6)	ND, ND
				Grain	117	ND, ND
				Straw	117	ND, ND
Wetaskiwin, AB; 2001 (TCI-01-007-19)	14	Barley; Rahigan	0.067	Hay	84 (8)	ND, ND
				Grain	132	ND, ND

TABLE C.3. Residue Data from Barley Field Trials with Quizalofop-P-Ethyl.

Trial ID (City, State; Year)	Zone	Crop; Variety	Total Rate (lb ai/A)	Commodity or Matrix	PHI [1] (days)	Total Quizalofop-P-Ethyl Residues (ppm)
				Straw	132	ND, ND
Minto, MB; 2001 (TC1-01-007-20)	14	Barley; AC Metcalf	0.069	Hay	75 (10)	ND, ND
				Grain	112	ND, ND
				Straw	112	ND, ND
Boissevain, MB; 2001 (TC1-01-007-21)	14	Barley; Robust	0.069	Hay	76 (10)	ND, ND
				Grain	106	ND, ND
				Straw	106	ND, ND
Lancombe, AB; 2001 (TC1-01-007-22)	14	Barley; CDC Dolly	0.070	Hay	75 (10)	ND, ND
				Grain	134	ND, ND
				Straw	134	ND, ND
Lancombe, AB; 2001 (TC1-01-007-23)	14	Barley; CDC Dolly	0.067	Hay	81 (9)	ND, ND
				Grain	134	ND, ND
				Straw	134	ND, ND
Rosthern, SK; 2001 (TC1-01-007-24)	14	Barley; CDC Sisler	0.069	Hay	55 (4)	ND, ND
				Grain	100	ND, ND
				Straw	100	ND, ND
Hepburn, SK; 2001 (TC1-01-007-25)	14	Barley; Metcalf	0.068	Hay	60 (4)	ND, ND
				Grain	98	ND, ND
				Straw	98	ND, ND

[1] The reported PHI for hay is from last application to cutting; the number of days samples were dried prior to collection is reported in parentheses.
[2] Less than the defined LOD (0.017 ppm).

TABLE C.4. Summary of Residue Data from Barley Field Trials with Quizalofop-P-Ethyl.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels [1] (ppm)						
			n	Min.	Max.	HAFT [2]	Median (STMdR) [3]	Mean (STMR) [4]	Std. Dev.
Barley, hay	0.066-0.070	48-219	50	<0.05	<0.05	<0.05	<0.025	<0.025	0
Barley, grain	0.066-0.070	90-255	50	<0.05	<0.05	<0.05	<0.025	<0.025	0
Barley, straw	0.066-0.070	90-255	50	<0.05	<0.05	<0.05	<0.025	<0.025	0

[1] The LOQ was 0.05 ppm and the LOD was 0.017 ppm for all barley matrices. In calculating the median, mean, and standard deviation, half the LOQ was used for residues reported below the LOQ in Table C.3.
[2] Highest Average Field Trial.
[3] Supervised Trial Median Residue
[4] Supervised Trial Mean Residue

D. CONCLUSION

The submitted barley field trial data reflect the use of a single preplant application of a 0.88 lb/gal EC formulation of quizalofop-P-ethyl at 0.066-0.070 lb ai/A, with a PHI of 48-219 days for barley hay, and 90-255 days for barley grain and straw. An acceptable method was used for quantitation of residues in/on barley hay, grain and straw.

E. REFERENCES

DP Barcode: D310869
Subject: PP# 0F6076: Storage Stability DER for Wheat
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885801.Der3

DP Barcode: D310869
Subject: PP# 0F6076: Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities
Reviewer: S. Oonnithan
Date: June 13, 2006
MRID: 45885803 and 45885804

F. DOCUMENT TRACKING

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

Quizalofop-P-ethyl/PC Code 128709/Nissan Chemical Industries, Ltd./33906
DACO 7.2.1, 7.2.2, and 7.2.3/OPPTS 860.1340/OECD IIA 4.2.5, 4.2.6 and 4.3
Residue Analytical Method -- Alfalfa, Barley, and Wheat Commodities

Primary Evaluator: S. Oonnithan, Biologist — Date: June 13, 2006
Registration Action Branch 2
Health effects Division (7509P)

Peer Reviewer: William Drew, Environmental Scientist — Date: June 13, 2006
Registration Action Branch 2
Health Effects Division (7509P)

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850. The DER has been reviewed by the Health Effects Division (HED) and revised to reflect the current Office of Pesticide Programs (OPP) policies.

STUDY REPORTS

45885803 Westberg, G. (2002) Validation of the Analytical Method for the Determination of Quizalofop-P-Ethyl and Quizalofop-P in Wheat, Barley and Alfalfa Raw Agricultural Commodities and Wheat Grain Processed Commodities: Lab Project Number: MLIR-02-01. Unpublished study prepared by Morse Laboratories, Inc. 84 p.

45885804 Faltynski, K. (2002) Independent Laboratory Validation (ILV) of Morse Method Meth-147 "Determination of Quizalofop-P-ethyl and Quizalofop-P in Wheat, Barley and Alfalfa Raw Agricultural Commodities and Wheat Grain Processed Commodities": Lab Project Number: 01-0040: MLIR-02-01: METH-147. Unpublished study prepared by EN-CAS Analytical Laboratories. 144 p.

EXECUTIVE SUMMARY

Nissan Chemical Industries, Ltd. has submitted an analytical method description and validation data for a data collection method, Morse Method Meth-147, for the determination of residues of quizalofop-P-ethyl and its acid metabolite quizalofop-P in alfalfa, raw agricultural commodities (RACs) of barley and wheat, and wheat processed commodities. The high performance liquid chromatography (HPLC) method, entitled "Determination of Quizalofop-P-Ethyl and Quizalofop-P in Wheat, Barley and Alfalfa Raw Agricultural Commodities and Wheat Grain Processed Commodities" was used to determine residues of quizalofop-P-ethyl and quizalofop-P in/on the following commodities from the storage stability, crop field trial, and processing studies associated with D310869: barley grain, hay, and straw; wheat forage, grain, hay, and straw; and wheat bran, flour, germ, middlings, and shorts.

The method is a modification of HPLC Method No. SARS-98-06, the data-collection method used for the determination of residues of quizalofop-P-ethyl and quizalofop-P in/on flax and sunflower commodities. In this method, samples are refluxed with methanolic potassium

hydroxide (KOH) to convert quizalofop-P-ethyl and quizalofop-P residues to 2-methoxy-6-chloroquinoxaline (MeCHQ). The solution is acidified and partitioned with hexane to extract the MeCHQ, and the hexane fraction is cleaned up by gel permeation chromatography (GPC); the hexane fractions of barley and wheat hay and straw and alfalfa forage and hay are cleaned up by silica solid-phase extraction (SPE) prior to GPC cleanup. The GPC eluate is concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Results are converted to quizalofop-P-ethyl or quizalofop-P equivalents using a molecular weight conversion factor. We note that results would only be converted to quizalofop-P equivalents for the purposes of calculating recovery in samples fortified with quizalofop-P. The validated limit of quantitation (LOQ) reported for the method is 0.05 ppm for all matrices.

Method validation data for HPLC Morse Method Meth-147 demonstrated adequate method recoveries of quizalofop-P-ethyl and quizalofop-P from wheat grain, forage, hay, straw, middlings, bran, and germ, and alfalfa forage and hay. Following fortification of samples with each analyte at 0.05 and 2.5 ppm, recoveries of quizalofop-P-ethyl and quizalofop-P averaged 86 ± 3.9% and 78 ± 3.8%, respectively, from alfalfa commodities, and 88 ± 7.8% and 81 ± 6.3%, respectively, from wheat commodities. Recoveries ranged 71-100% for quizalofop-P-ethyl and 70-96% for quizalofop-P.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for barley commodities. Concurrent method recovery data were included with the barley crop field trial study submitted in conjunction with D310869; adequate recoveries of quizalofop-P-ethyl and quizalofop-P were obtained from barley hay, grain, and straw fortified with each analyte at 0.05-0.2 ppm. The concurrent method recovery data in combination with the method validation data are sufficiently representative of the expected residue levels for the barley and wheat commodities included in the petition associated with D310869.

The petitioner has proposed the current HPLC/UV enforcement method (Dupont Method AMR-153-83, Revision 3, January 1987; MRID 40322410) as a confirmatory method for the HPLC data-collection method.

A successful independent laboratory validation (ILV) trial was conducted using samples of wheat straw fortified with quizalofop-P-ethyl and quizalofop-P at 0.05, 0.10, and 6.5 ppm each. No radiovalidation data were submitted for the method. Because the extraction procedures of the method are relatively rigorous, no radiovalidation data will be required to support the method.

We note that the method description did not address the issue of determination of the S enantiomers of quizalofop-ethyl and quizalofop. Because the KOH hydrolysis step would convert both the R and S enantiomers of quizalofop-ethyl and quizalofop to MeCHQ, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the analytical method test data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, D310869.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Quizalofop-P-ethyl is a selective herbicide intended for the control of annual and perennial grasses in noncrop and cropped areas. Applications are to be made preplant, preemergence, or postemergence. Quizalofop-P-ethyl is a racemic mixture of R and S enantiomers and the R-enantiomer is the pesticidally active isomer. The nomenclature and physicochemical properties are summarized in Tables 1 and 2.

TABLE A.1. Test Compound Nomenclature.

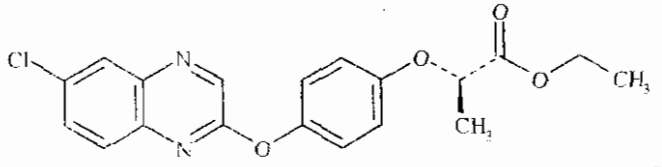
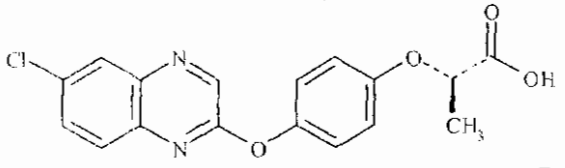
Chemical structure	
Common name	Quizalofop-P-ethyl
Company experimental name	Not provided
IUPAC name	ethyl (R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propanoate
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid, ethyl ester
CAS registry number	100646-51-3
End-use product (EP)	0.88 lb/gal EC formulation (EPA Reg. No. 33906-9)
Chemical structure	
Common name	Quizalofop-P
Company experimental name	Not provided
IUPAC name	(R)-2-[4-((6-chloroquinoxalin-2-yl)oxy)phenoxy]propionic acid
CAS name	(2R)-2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoic acid
CAS registry number	94051-08-8
End-use product (EP)	Not applicable

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound Quizalofop-P-Ethyl.		
Parameter	Value	Reference
Melting point	76.0-77.0 °C (pure form)	CB Nos. 5852 & 5853, 3/29/90, W. Hazel
pH	6.6 (1% aqueous slurry)	
Density	1.35 g/cm^3 at 20 °C (pure form)	
Water solubility	0.4 ppm (20 °C)	
Solvent solubility	g/L at 20 °C	
	acetone 650	
	benzene 680	
	carbon disulfide 660	
	chloroform 1350	
	cyclohexanone 440	
	dichloromethane 1970	
	dimethyl sulfoxide 200	
	ethanol 22	
	n-hexane 5	
	methanol 22	
	tetrahydrofuran 1160	
	toluene 430	
	xylene 360	
Vapor pressure	8.3 x 10^{-10} mm Hg (20 °C)	
Dissociation constant, pK_a	Not applicable	
Octanol/water partition coefficient	log P_{OW} = 4.66	
UV/visible absorption spectrum	Not available	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

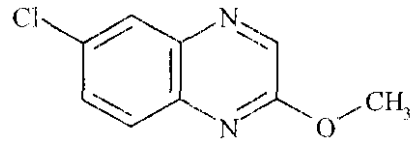
A data-gathering method, HPLC Morse Method Meth-147, entitled "Determination of Quizalofop-P-Ethyl and Quizalofop-P in Wheat, Barley and Alfalfa Raw Agricultural Commodities and Wheat Grain Processed Commodities," was used to determine residues of quizalofop-P-ethyl and quizalofop-P in/on the following commodities from the storage stability, crop field trial, and processing studies on barley grain, hay, and straw; wheat forage, grain, hay, and straw; and wheat bran, flour, germ, middlings, and shorts.

This HPLC Morse Method Meth-147 is a modification of HPLC Method No. SARS-98-06, used for the data-collection of quizalofop-P-ethyl and quizalofop-P residues in/on flax and sunflower commodities (D310869, DER for Residue Analytical Method – Sunflower Seed, Meal, and Oil, MRID 44967003 and 44967704).

B.1.1. Principle of the Method

Briefly, samples are refluxed with methanolic KOH to convert quizalofop-P-ethyl and quizalofop-P residues to MeCHQ (see structure below). The solution is acidified and partitioned with hexane to extract the MeCHQ. Then the hexane fraction is cleaned up by GPC; the hexane fractions of matrices are cleaned up by silica SPE prior to GPC cleanup. The GPC eluate is

Structure of MeCHQ:



concentrated and redissolved in acetonitrile/water for HPLC analysis with fluorescence detection. Results are converted to parent or quizalofop-P equivalents using molecular weight conversion factors; 1.917 for quizalofop-P-ethyl and 1.773 for quizalofop-P. We note that results would only be converted to quizalofop-P equivalents for the purposes of calculating recovery in samples fortified with quizalofop-P. A summary of the analytical method used here is provided in Table B.1.1.

TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Wheat and Barley Raw Agricultural and Processed Commodities	
Method ID	Morse Method Meth-147 (dated 1/10/02)
Analytes	Quizalofop-P-ethyl, quizalofop-P, and the S enantiomers
Extraction solvent/technique	*Samples are refluxed with 1 N methanolic KOH for 1.5 h. Water and saturated sodium chloride solution are added, and the mixture is acidified to pH 2.0 using concentrated hydrochloric acid. The extract is partitioned with hexane (2x), and the hexane phase is dried with sodium sulfate and then concentrated after the addition of 1% decanol in hexane.*
Cleanup strategies	Wheat and barley grain, wheat forage, and wheat processed commodities: The hexane fraction is concentrated to near dryness, redissolved in dichloromethane, and cleaned up by GPC. The eluate is evaporated to dryness after the addition of 25% ethylene glycol in methanol, and redissolved in acetonitrile:water (1:1, v:v). Wheat hay and straw, barley hay and straw, and alfalfa forage and hay: The hexane fraction is cleaned up on a silica SPE cartridge, using hexane:ethyl acetate (9:1, v:v) to elute residues. The eluate is concentrated to near dryness after the addition of 1% decanol in hexane, and then redissolved in dichloromethane and subjected to GPC cleanup as described above for wheat grain.
Instrument/Detector	HPLC with fluorescence detection, using a reversed phase column and a gradient mobile phase of acetonitrile and water. The fluorescence detector uses an excitation setting of 338 nm and an emission setting of 374 nm.
Standardization method	External standardization, using calibration standards of MeCHQ to generate a standard curve through linear regression. Results are converted to quizalofop-P-ethyl or quizalofop-P equivalents using molecular weight conversion factors.
Stability of std solutions	*Stock solutions of quizalofop-P-ethyl, quizalofop-P, and* MeCHQ are to be stored in amber bottles at -22 to -8 °C and to be prepared fresh every 3 months (MeCHQ) or 6 months (quizalofop-P-ethyl and quizalofop-P). Fortification and calibration solutions are to be stored in amber bottles at 1 to 8 °C and prepared fresh every month.
Retention times	~14.6-16.5 minutes

B.2. Enforcement Method

The petitioner has not proposed the current data-collection method (HPLC Morse Method Meth-147) for enforcement purposes. However, the Agency has submitted the LAN-1 HPLC-UV method (DuPont Method AMR 1853-90) for a Tolerance Method Validation (D215499, Griffith, F., 10/11/95). The Analytical Chemistry Branch (ACB) has pointed out several deficiencies in the LAN-1 HPLC-UV method, which the registrant have not yet been addressed (D226691, Griffith, F., 06/17/96).

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Characteristics of the method used for the quantitation of residues of quizalofop-P-ethyl and quizalofop-P in/on wheat (HPLC Morse Method Meth-147) is summarized in Table C.1.1.

TABLE C.1.1. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Wheat.

Analytes	Quizalofop-P-ethyl, quizalofop-P, and the S enantiomers
Equipment [1]	Thermo Separation Products SP8800 Tenary Gradient Pump attached to a Thermo Separation Products LC 304 Fluorescence Detector; Supelco Discovery® RP Amide C16 column (25 cm x 4.6 mm, 5 micron particle size; for wheat and barley grain, wheat forage, and wheat processed commodities); or a Zorbax® Bonus RP column (25 cm x 4.6 mm, 5 micron particle size; for wheat hay and straw, barley hay and straw, and alfalfa forage and hay)
Limit of quantitation (LOQ)	0.05 ppm for wheat, barley, and alfalfa raw agricultural commodities and wheat grain processed commodities (determined as lowest fortification level with adequate recovery)
Limit of detection (LOD)	0.017 ppm (defined as 1/3 the LOQ)
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision at 0.05 and 2.5 ppm for wheat and alfalfa commodities. Recovery ranges (and CVs) from these matrices were 71-100% (4.2-13) for quizalofop-P-ethyl and 70-96% (3.1-12) for quizalofop-P. See Table C.1.1 above.
Reliability of the Method [ILV]	An independent laboratory method validation (ILV) was conducted to verify the reliability of Morse Method Meth-147 for the determination of quizalofop-P-ethyl and quizalofop-P in wheat straw. The values obtained indicate that Morse Method Meth-147 is reliable; see Section C.3.
Linearity	The method/detector response was linear (coefficient of determination, r^2= 1.0) within the range 0.04-0.6 ppm.
Specificity	The control chromatograms provided generally had no peaks above the chromatographic background, and the spiked sample chromatograms contained only the analyte peak of interest near the retention time of MeCHQ. Peaks were well defined and symmetrical.

TABLE C.1.2. Recovery Results from Method Validation of Wheat and Alfalfa RAC and Wheat Grain *Processed Commodities using the* Data-Gathering Analytical Method.

Matrix	Analyte [1]	Spiking Level (ppm)	Individual Recoveries (%)	Recovery (%)		
				Mean	SD[2]	CV[3]
Wheat grain	Quizalofop-P-ethyl	0.05	80, 82, 90	85	4.1	4.8
		2.5	84, 86, 90			
	Quizalofop-P	0.05	81, 81, 83	79	3.9	5.0
		2.5	72, 77, 79			
Wheat forage	Quizalofop-P-ethyl	0.05	99, 100, 100	94	8.0	8.5
		2.5	83, 84, 95			
	Quizalofop-P	0.05	90, 90, 96	84	9.6	12
		2.5	71, 76, 80			
Wheat hay	Quizalofop-P-ethyl	0.05	87, 88, 99	92	4.5	4.9
		2.5	89, 92, 94			
	Quizalofop-P	0.05	82, 83, 86	84	2.6	3.1
		2.5	80, 84, 87			
Wheat straw	Quizalofop-P-ethyl	0.05	80, 86, 94	86	5.4	6.2
		2.5	82, 84, 91			
	Quizalofop-P	0.05	82, 83, 88	82	3.6	4.4
		2.5	78, 79, 80			
Wheat middlings	Quizalofop-P-ethyl	0.05	71, 81, 96	80	8.9	11
		2.5	74, 77, 84			
	Quizalofop-P	0.05	70, 74, 82	74	4.2	5.7
		2.5	71, 74, 75			
Wheat grain bran	Quizalofop-P-ethyl	0.05	77, 77, 81	88	11	13
		2.5	97, 99, 100			
	Quizalofop-P	0.05	71, 76, 76	80	7.0	8.7
		2.5	86, 87, 87			
Wheat grain germ	Quizalofop-P-ethyl	0.05	81, 88, 91	90	5.0	5.6
		2.5	91, 92, 96			
	Quizalofop-P	0.05	76, 81, 82	84	6.3	7.4
		2.5	86, 88, 94			
Alfalfa forage	Quizalofop-P-ethyl	0.05	86, 88, 95	87	4.5	5.2
		2.5	82, 84, 85			
	Quizalofop-P	0.05	78, 79, 87	80	3.7	4.6
		2.5	77, 78, 80			
Alfalfa hay	Quizalofop-P-ethyl	0.05	80, 86, 91	86	3.6	4.2
		2.5	84, 86, 86			
	Quizalofop-P	0.05	72, 73, 76	75	2.5	3.3
		2.5	75, 78, 78			

[1] Standards were prepared in acetonitrile for quizalofop-P-ethyl and in 0.2 % acetic acid in acetonitrile for quizalofop-P analytes.
[2] Standard deviation
[3] Coefficient of variation

The method validation recoveries of quizalofop-P-ethyl and quizalofop-P using HPLC Morse Method Meth-147 were adequate from fortified samples of wheat grain, forage, hay, straw, middlings, bran, and germ, and alfalfa forage and hay (Table C.1.2). Following fortification of

samples with each analyte at 0.05 and 2.5 ppm, mean recoveries of quizalofop-P-ethyl and quizalofop-P averaged 86% and 78%, respectively, from alfalfa commodities, and 88% and 81%, respectively, from wheat commodities. Individual recoveries ranged 71-100% for quizalofop-P-ethyl and 70-96% for quizalofop-P.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for barley commodities. Concurrent method recovery data were included with the barley crop field study submitted in conjunction with D310869, 45885802.der); adequate recoveries of quizalofop-P-ethyl and quizalofop-P were obtained from barley hay, grain, and straw fortified with each analyte at 0.05-0.2 ppm. The concurrent recovery validation data in combination with the method validation data are sufficiently representative of the expected residue levels for the barley and wheat commodities .

The petitioner has proposed the current HPLC/UV enforcement method (Dupont Method AMR-153-83, Revision 3, January 1987; MRID 40322410) as a confirmatory method for the HPLC data-collection method.

No radiovalidation data were submitted for the method. Because the extraction procedures of the method are relatively rigorous (reflux in 1 N KOH in methanol for 1.5 hours), no radiovalidation data will be required to support the method.

We note that the method description did not address the issue of determination of the S enantiomers of quizalofop-ethyl and quizalofop. Because the KOH hydrolysis step would convert both the R and S enantiomers of quizalofop-ethyl and quizalofop to MeCHQ, all reported results for total quizalofop-P-ethyl residues would include residues of both the R and S enantiomers of quizalofop-ethyl and quizalofop.

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Wheat,

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Quizalofop-P-Ethyl and Quizalofop-P Residues in Wheat,	
Analytes	Quizalofop-P-ethyl, quizalofop-P, and the S enantiomers
Equipment ID	Thermo Separation Products SP8800 Tenary Gradient Pump attached to a Thermo Separation Products LC 304 Fluorescence Detector; Supelco Discovery® RP Amide C16 column (25 cm x 4.6 mm, 5 micron particle size; for wheat and barley grain, wheat forage, and wheat processed commodities); or a Zorbax® Bonus RP column (25 cm x 4.6 mm, 5 micron particle size; for wheat hay and straw, barley hay and straw, and alfalfa forage and hay)
Limit of quantitation (LOQ)	0.05 ppm for wheat, barley, and alfalfa raw agricultural commodities and wheat grain processed commodities (determined as lowest fortification level with adequate recovery)
Limit of detection (LOD)	0.017 ppm (defined as 1/3 the LOQ)
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision at 0.05 and 2.5 ppm for wheat and alfalfa commodities. Recovery ranges (and CVs) from these matrices were 71-100% (4.2-13) for quizalofop-P-ethyl and 70-96% (3.1-12) for quizalofop-P. See Table C.1.1 above.
Reliability of the Method [ILV]	An independent laboratory method validation (ILV) was conducted to verify the reliability of Morse Method Meth-147 for the determination of quizalofop-P-ethyl and quizalofop-P in wheat straw. The values obtained indicate that Morse Method Meth-147 is reliable; see Section C.3.
Linearity	The method/detector response was linear (coefficient of determination, $r^2 = 1.0$) within the range 0.04-0.6 ppm.
Specificity	The control chromatograms provided generally had no peaks above the chromatographic background, and the spiked sample chromatograms contained only the analyte peak of interest near the retention time of MeCHQ. Peaks were well defined and symmetrical.

C.2. Enforcement Method

The petitioner has not proposed the submitted data-collection method (HPLC Morse Method Meth-147) for enforcement purposes.

C.3. Independent Laboratory Validation

An independent laboratory validation (ILV; MRID 45885804) of HPLC Morse Method Meth-147 was conducted by EN-CAS Analytical Laboratories (Winston-Salem, NC) using samples of wheat straw.

Samples of untreated wheat straw (pre-ground control samples supplied by Morse Laboratories) were fortified, in separate aliquots, with quizalofop-P-ethyl and quizalofop-P at 0.05 ppm (LOQ), 0.10 ppm, and 6.5 ppm. Fortified and unfortified samples were analyzed using HPLC Morse Method Meth-147 as described in Table B.1.1. The petitioner noted that wheat straw was chosen as the test material in this study because it is one of the most difficult matrices to analyze.

The first and second ILV trials failed due to problems in the final evaporation step in the method (in the first trial, two separate phases were found to have formed in the HPLC injection vial; and in the second trial, two separate phases were found even after the evaporation step was closely monitored). Recoveries of quizalofop-P-ethyl and quizalofop-P were 32-53% and 27-67%, respectively, in trial 1 and 51-61% and 55-129%, respectively, in trial 2. The ILV laboratory contacted Morse Laboratories after the second trial to discuss the final evaporation step of the

method. On the third trial, the ILV laboratory tried a different solvent exchange procedure for this final step, and the third trial was successful. The recoveries of quizalofop-P-ethyl and quizalofop-P from wheat straw samples in the third trial are reported in Table C.3.1. Total quizalofop-P-ethyl and quizalofop-P residues were below the LOQ (<0.05 ppm) in two samples each of unfortified wheat straw. The laboratory reported that, other than the solvent exchange modification described above, the method was followed as written with minor modifications in the type of equipment used and the volumes of solvents used to elute residues from the GPC and SPE columns.

TABLE C.3.1. Results of an Independent Laboratory Validation of the Data Gathering Method (HPLC Morse Meth-147) for the Determination of Quizalofop-P-Ethyl and Quizalofop-P in Wheat Straw.

Matrix	Analyte	Spiking Level (ppm)	Individual Recoveries(%)	Recovery (%)		
				Mean	SD [1]	CV [2]
Wheat straw	Quizalofop-P-ethyl	0.05	102, 102	97	8.1	8.4
		0.10	96, 101			
		6.5	81, 100			
	Quizalofop-P	0.05	94, 102	96	3.5	3.6
		0.10	94, 97			
		6.5	92, 95			

[1] Standard deviation
[2] Coefficient of variation

The laboratory reported that a set of six samples could be prepared and analyzed by HPLC in approximately 2.5 eight-hour days. The ILV laboratory did not note any critical steps or recommend any method modifications.

D. CONCLUSION

Adequate method validation data have been submitted for the HPLC Morse Method Meth-147 for determination of residues of quizalofop-P-ethyl and quizalofop-P in alfalfa, barley, and wheat raw agricultural commodities and wheat processed commodities and the data are sufficiently representative of the expected residue levels for the wheat commodities. The method was also used for data collection purposes for the analysis of barley hay, grain, and straw samples from the barley field trial studies and adequate concurrent method validation data were submitted for barley commodities.

The petitioner is not proposing the HPLC Morse Method Meth-147 used for data collection for enforcement purposes. No radiovalidation data have been submitted for the method; however, radiovalidation data are not required because the extraction procedures are rigorous. Adequate independent laboratory validation data have been submitted for the method using samples of wheat straw.

E. REFERENCES

DP Barcode: D219639
Subject: PP# 3F4268 - Quizalofop-P-Ethyl ester (Assure® II) on Legume Vegetables and Foliage of Legume Vegetables of Legume Vegetables Crop Groups, Sugarbeet Tops, Roots, Molasses, and Cottonseed. Evaluation of the Analytical Chemistry Laboratory Pre-review of the Tolerance Method Validations for Quizalofop-P-Ethyl Ester.
From: F. Griffith
Date: 10/11/95
MRID: 43804101

DP Barcode: D226691
Subject: PP# 3F4268/5H5720 - Quizalofop-P-Ethyl ester (Assure® II) on the Legume Vegetables and Foliage of Legume Vegetables Crop Groups, Sugarbeet Tops, Roots, Molasses, and Cottonseed.
From: F. Griffith
Date: 6/17/96
MRID: None

DP Barcode: D310869
Subject: PP# 0F6076, DER for Residue Analytical Method – Alfalfa, Barley, and Wheat Commodities.
From: S. Oonnithan
Date: June 13, 2006
MRIDs: 45885803 and 45885804.

F. *DOCUMENT TRACKING*

Reviewer: S. Oonnithan
Date: June 13, 2006
Petition Number: PP# 0F6076
EPA Reg. No. 33906-9
DP Barcode: D310869
PC Code: 128709

13544

R142437

Chemical: Propanoic acid, 2-?4-?(6-chloro-2-quinoxalinyl)oxyphenoxyU-, ethylester, (R)-

PC Code: 128709
HED File Code: 11000 Chemistry Reviews
Memo Date: 7/24/2006
File ID: DPD266204
Aecession #: 000-00-0119

HED Records Reference Center
4/24/2007